THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[SEVENTH SERIES.]

MARCH 1935.

XLV. *The Action of a Rivet in a Plate of Finite Breadth.*

By R. C. KNIGHT, *University College, Southampton* *.

Introduction.

THE problem of determining, on the basis of the General Theory of Elasticity, the stresses produced in a flat plate by a rivet is one of considerable difficulty. This is due to two circumstances of quite different natures. On the one hand there is the uncertainty as to the way in which the rivet bears upon the hole in which it has been placed. On the other there is the effect on the stresses of neighbouring rivets or boundaries of the plate. In the present paper we shall be concerned with the second of these difficulties. Having first postulated the action of the rivet on the hole, we shall compare the resulting stresses when the plate is of infinite extent with those when the plate is a strip of finite breadth.

We first consider the rivet isolated and indefinitely far from all boundaries. It is pulled in a given direction, and a likely form of the pressure between the rivet and the hole is assumed. The stresses are then determined by known methods of biharmonic analysis. Our results bear a close resemblance to those obtained by Bickley†, who considered

* Communicated by Prof. R. C. J. Howland, M.A., D.Sc.

† Phil. Trans. A, vol. ccvii. pp. 383–415 (1928).

several types of boundary conditions on the rivet-hole. He compared his results with those obtained by Coker * by photo-elastic methods, and found a good measure of agreement.

Next we take the case of a rivet in a hole whose diameter is half the breadth of a strip. To obtain the stresses on the hole when the rivet is pulled in a given direction we adopt a method used by Howland †, who assumed them to be produced by an isolated force acting at the centre of the rivet. The solution for such a force has been given by Howland and Stevenson ‡, while the approximation method used by them has been adopted to determine the stresses after the action of the rivet has been assumed. This method was given in an earlier paper by Howland §.

Two distinct cases have been considered: first, when the rivet is pulled in a direction parallel with the edges of the strip; and second, when the direction of the pull is perpendicular. In each of these cases two sets of results have been worked out, corresponding to different conditions at the ends of the strip.

The Rivet in an Infinite Plate.

We consider a uniform plate of elastic material whose boundaries are at an infinite distance from the centre of a circular hole. Taking the centre of this circle as origin of Cartesian coordinates, we define polars by

$$x=r\sin\theta, \quad y=r\cos\theta. \quad . \quad . \quad . \quad . \quad (1.1)$$

This follows the practice adopted in "A" and "B," and will be found advantageous later.

If a is the radius of the hole, we write

$$r'=r/a, \quad x'=x/a, \quad y'=y/a. \quad . \quad . \quad . \quad (1.2)$$

We suppose the material to be in a state of "generalised plane stress" || corresponding to a stress-function χ

* Jour. Franklin Inst. vol. cxcix. (1925).

† Third International Cong. of App. Mechanics, Stockholm, 1930.

‡ Phil. Trans. A, vol. ccxxxii. pp. 155–222 (1933). This paper will be referred to as "A."

§ Phil. Trans. A, vol. ccxxix. pp. 49–86 (1930). This paper will be referred to as "B."

|| See Filon, Phil. Trans. A, vol. cci. p. 67 (1903); also Love, 'Theory of Elasticity,' 4th ed. p. 138 (Cambridge, 1927).

satisfying the equation

$$\nabla^4\chi \equiv \frac{\partial^4\chi}{\partial x^4} + 2\frac{\partial^4\chi}{\partial x^2\partial y^2} + \frac{\partial^4\chi}{\partial y^4} = 0. \quad . \quad . \quad (1.3)$$

Let $$\chi = \chi' + \chi'', \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1.4)$$

where χ', χ'' both satisfy (1.3), and χ' corresponds to a force P acting at the origin in the direction of Ox, assuming the circle to be filled in with a disk of elastic material. χ' then has the form

$$\chi' = \frac{Pa}{4\pi}\left[\frac{1-2\sigma}{1-\sigma} r' \sin\theta \log r' + 2\theta r' \cos\theta\right]. \quad . \quad (1.5)$$

This force P will cause the disk to act on the hole with certain pressures and shears. These will be given later. If we regard only the right-hand half of the circle, they represent quite plausibly the tractions exerted by a rivet pulled in direction Ox. We now determine χ'' so that it cancels the tractions due to χ' on the left-hand half of the circle, but doubles them on the right-hand half. This gives the particular rivet action which we shall consider.

The symbol σ in (1.5) is the modified Poisson's ratio occurring in generalized plane stress. Its value is usually about 0·2 to 0·25. We shall take the value $\sigma = 0{\cdot}25$. A different value would not modify the results to any great extent, and the effect of changing it will be discussed later.

The stresses due to χ' are

$$\widehat{rr'} = \frac{1}{a^2}\left(\frac{1}{r'^2}\frac{\partial^2\chi'}{\partial\theta^2} + \frac{1}{r'}\frac{\partial\chi'}{\partial r'}\right)$$

$$= -\frac{P}{2\pi a}\left[\frac{3-2\sigma}{2(1-\sigma)}\frac{\sin\theta}{r'}\right] \quad . \quad . \quad . \quad (1.6)$$

$$\widehat{\theta\theta'} = \frac{1}{a^2}\frac{\partial^2\chi'}{\partial r'^2},$$

$$= \frac{P}{2\pi a}\left[\frac{1-2\sigma}{2(1-\sigma)}\frac{\sin\theta}{r'}\right] \quad . \quad . \quad . \quad (1.7)$$

$$\widehat{r\theta'} = -\frac{1}{a^2}\frac{\partial}{\partial r'}\left(\frac{1}{r'}\frac{\partial\chi'}{\partial\theta}\right),$$

$$= -\left[\frac{P}{2\pi a}\frac{1-2\sigma}{2(1-\sigma)}\frac{\cos\theta}{r'}\right]. \quad . \quad . \quad . \quad (1.8)$$

Putting $r'=1$ and $\sigma=0{\cdot}25$, we get the values of the stresses due to χ' on the rim of the hole. These have been tabulated for θ at intervals of 15° around the circle. They are given here for θ in the first quadrant only, for since $\widehat{rr'}$ and $\widehat{\theta\theta'}$ are odd in x and even in y, while $\widehat{r\theta'}$ is odd in y and even in x, their values in the other quadrants are easily found. If

$$\widehat{rr'}=-\frac{P}{\pi a}u, \quad \widehat{\theta\theta'}=\frac{P}{\pi a}v, \quad \widehat{r\theta'}=-\frac{P}{\pi a}w;$$

the values of u, v, w are given in Table I.

TABLE I.

θ°.	u.	v.	w.
0	0	0	0·16667
15	0·21568	0·04314	0·16099
30	0·41667	0·08333	0·14434
45	0·58926	0·11785	0·11785
60	0·72169	0·14434	0·08333
75	0·80494	0·16099	0·04314
90	0·83333	0·16667	0

In order to obtain χ'' we must first express the boundary conditions in a suitable form. To do this we may take values of $\widehat{rr'}$ and $\widehat{r\theta'}$ as given by equations (1.6) and (1.8) and re-expand $\widehat{rr'}$ in a Fourier cosine series and $\widehat{r\theta'}$ in a Fourier sine series. These series will represent functions identical with (1.6) and (1.8) over the range $0<\theta<\pi$, but differing in sign over the range $\pi<\theta<2\pi$. They therefore give appropriate boundary conditions for the stresses due to χ''. The resulting series for $\widehat{rr''}$ and $\widehat{r\theta''}$ are not, however, rapidly convergent, and this would greatly increase the labour of subsequent calculations. An alternative method, which we shall use, is that of finite Fourier series.

Convenient formulæ for the coefficients of such a series are given by Whittaker and Robinson *, following Runge. Here we have some simplification on account of symmetry. If we write $u_0, u_1, \ldots u_6$ for the values of u at $\theta=0°$, $15°\ldots90°$ and $w_0, w_1, \ldots w_6$ for the values of w at these points, then we may easily show that

$$\left.\begin{aligned} u&=A_0+A_2\cos 2\theta+\ldots+A_{12}\cos 12\theta,\\ w&=B_2\sin 2\theta+\ldots+B_{10}\sin 10\theta, \end{aligned}\right\} \quad . . \quad (1.9)$$

* 'The Calculus of Observations,' chap. x. (1924.)

where

$$\left.\begin{aligned}
A_0&=\frac{1}{12}\{u_0+2(u_1+u_2+u_3+u_4+u_5)+u_6\},\\
A_2&=\frac{1}{6}\{u_0+u_2-u_4-u_6+\sqrt{3}(u_1-u_5)\},\\
A_4&=\frac{1}{6}\{u_0+u_1-u_2-2u_3-u_4+u_5+u_6\},\\
A_6&=\frac{1}{6}\{u_0-2u_2+2u_4-u_6\},\\
A_8&=\frac{1}{6}\{u_0-u_1-u_2+2u_3-u_4-u_5+u_6\},\\
A_{10}&=\frac{1}{6}\{u_0+u_2-u_4-u_6-\sqrt{3}(u_1-u_5)\},\\
A_{12}&=\frac{1}{12}\{u_0-2(u_1-u_2+u_3-u_4+u_5)+u_6\},\\
B_2&=\frac{1}{6}\{w_1+2w_3+w_5+\sqrt{3}(w_2+w_4)\},\\
B_4&=\frac{\sqrt{3}}{6}\{w_1+w_2-w_4-w_5\},\\
B_6&=\frac{1}{3}\{w_1-w_3+w_5\},\\
B_8&=\frac{\sqrt{3}}{6}\{w_1-w_2+w_4-w_5\},\\
B_{10}&=\frac{1}{6}\{w_1+2w_3+w_5-\sqrt{3}(w_2+w_4)\}.
\end{aligned}\right\}\quad .\ (1.10)$$

The numerical values of these coefficients are given in Table II.

TABLE II.

n.	0.	1.	2.	3.	4.	5.	6.
A_{2n} ...	0·5275	−0·3598	−0·0772	−0·0372	−0·0245	−0·0196	−0·0091
B_{2n} ...	—	0·3190	0·0516	0·0288	0·0164	0·0076	—

The stresses on $r'=1$ due to χ'' are now

$$\widehat{rr''}=-\frac{P}{\pi a}\sum_{n=0}^{6}A_{2n}\cos 2n\theta, \qquad \widehat{r\theta''}=-\frac{P}{\pi a}\sum_{n=1}^{5}B_{2n}\sin 2n\theta. \quad . \quad . \quad . \quad (1.11)$$

The function χ'' will be even in both x and y, and will have the form

$$\chi''=\frac{Pa}{\pi}\left[-D_0\log r'+\sum_{n=1}^{\infty}\left(\frac{D_{2n}}{r'^{2n}}+\frac{E_{2n}}{r'^{2n-2}}\right)\cos 2n\theta\right]. \quad (1.12)$$

Its stresses will be

$$\widehat{rr''}=-\frac{P}{\pi a}\left[\frac{D_0}{r'^2}+2\sum_{n=1}^{\infty}\left\{\frac{n(2n+1)D_{2n}}{r'^{2n+2}}+\frac{(n+1)(2n-1)E_{2n}}{r'^{2n}}\right\}\cos 2n\theta\right], \quad (1.13)$$

$$\widehat{\theta\theta''}=\frac{P}{\pi a}\left[\frac{D_0}{r'^2}+2\sum_{n=1}^{\infty}\left\{\frac{n(2n+1)D_{2n}}{r'^{2n+2}}+\frac{(n-1)(2n-1)E_{2n}}{r'^{2n}}\right\}\cos 2n\theta\right], \quad (1.14)$$

$$\widehat{r\theta''}=-\frac{2P}{\pi a}\sum_{n=1}^{\infty}\left\{\frac{n(2n+1)D_{2n}}{r'^{2n+2}}+\frac{n(2n-1)E_{2n}}{r'^{2n}}\right\}\sin 2n\theta. \quad . \quad . \quad . \quad (1.15)$$

The equations (1.13), (1.15) when $r'=1$ must be identical with equations (1.11), so that, equating coefficients, we obtain

$$D_{2n}=\frac{(n+1)B_{2n}-nA_{2n}}{2n(2n+1)}, \quad (n\geq 1), \quad D_0=A_0\,; \quad (1.16)$$

$$E_{2n}=\frac{A_{2n}-B_{2n}}{2(2n-1)}, \quad (n\geq 1). \quad . \quad . \quad . \quad . \quad . \quad . \quad (1.17)$$

Their numerical values are tabulated in Table III.

TABLE III.

n.	0.	1.	2.	3.	4.	5.	6.
D_{2n} ...	0·5275	0·1063	0·0155	0·00540	0·00250	0·00131	0·00035
E_{2n} ...	—	−0·2494	−0·0215	−0·00660	−0·00292	−0·00151	−0·00041

This completes the determination of the stress function for the rivet in an infinite plate.

The Rivet in a Strip of Finite Breadth. Longitudinal Force.

As before, we let

$$\chi = \chi' + \chi'',$$

where now χ' corresponds to an isolated force P at the origin acting longitudinally, *i. e.*, in a direction Ox. Such a function has been given in "A," p. 159, and is

$$\chi' = \frac{Pb}{4\pi(1-\sigma)}\Big[(1-2\sigma)\xi \log \rho + 2(1-\sigma)\eta\theta + 2\sum_{n=0}^{\infty}({}^{a}a_n + {}^{a}b_n\rho^2)\rho^{2n+1}\sin(2n+1)\theta\Big], \quad (2.1)$$

TABLE IV.

n.	0.	1.	2.	3.	4.	5.	6.
$\frac{{}^{a}a_n}{1-\sigma}\cdots$	$\left.\begin{matrix}\\0\\\end{matrix}\right\}\left\{\begin{matrix}\\-1\cdot847\times10^{-2}\\\end{matrix}\right.$	$-9\cdot852\times10^{-2}$	$-1\cdot045\times10^{-2}$	$-1\cdot781\times10^{-3}$	$-3\cdot316\times10^{-4}$	$-6\cdot581\times10^{-5}$	$-1\cdot363\times10^{-5}$
$\frac{{}^{a}b_n}{1-\sigma}\cdots$		$1\cdot912\times10^{-2}$	$6\cdot706\times10^{-3}$	$1\cdot929\times10^{-3}$	$5\cdot186\times10^{-4}$	$1\cdot355\times10^{-4}$	$3\cdot487\times10^{-5}$

where $2b$ is the width of the strip, the circle being symmetrically placed between its straight edges. We have written

$$\xi = x/b, \quad \eta = y/b, \quad \rho = r/b. \quad . \quad . \quad . \quad (2.2)$$

We shall also write

$$\lambda = a/b, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.3)$$

and in our subsequent calculations have taken $\lambda = \frac{1}{2}$, this corresponding to a size of hole not likely to be exceeded in practice.

The coefficients ${}^{a}a_n$, ${}^{a}b_n$ are functions of integrals whose numerical values have been given ("B," p. 67), and also of σ. When $\sigma = 0\cdot2$ these coefficients are given in "A," p. 174; here we require them for $\sigma = 0\cdot25$. They are given in Table IV.

The stresses due to χ' at the rim of the hole $\rho=\lambda$ are

$$\widehat{rr}'=\frac{P}{2\pi(1-\sigma)b}\sum_{n=0}^{\infty} p_n \sin(2n+1)\theta, \quad . \quad . \quad (2.4)$$

$$\widehat{\theta\theta}'=\frac{P}{2\pi(1-\sigma)b}\sum_{n=0}^{\infty} q_n \sin(2n+1)\theta, \quad . \quad . \quad (2.5)$$

$$\widehat{r\theta}'=\frac{P}{2\pi(1-\sigma)b}\sum_{n=0}^{\infty} r_n \cos(2n+1)\theta, \quad . \quad . \quad (2.6)$$

where

$$\left.\begin{aligned}
p_0&=-\frac{3-2\sigma}{2\lambda}+2b_0\lambda,\\
p_n&=-\{2n(2n+1)a_n+(2n-1)(2n+2)b_n\lambda^2\}\lambda^{2n-1}, \quad (n>0).\\
q_0&=\frac{1-2}{2\lambda}+6b_0\lambda,\\
q_n&=\{2n(2n+1)a_n+(2n+2)(2n+3)b_n\lambda^2\}\lambda^{2n+1}, \quad (n>0),\\
r_0&=-\frac{1-2\sigma}{2\lambda}-2b_0\lambda,\\
r_n&=-\{2n(2n+1)a_n+(2n+1)(2n+2)b_n\lambda^2\}\lambda^{2n-1}, \quad (n>0).
\end{aligned}\right\} \quad . \quad . \quad . \quad (2.7)$$

TABLE V.

$\theta°$.	u.	v.	w.
0	0	0	0·3599
15	0·6419	−0·0350	0·4327
30	1·3797	0·0499	0·5798
45	2·1848	0·2701	0·6600
60	2·9206	0·5433	0·5804
75	3·4337	0·7609	0·3387
90	3·6171	0·8429	0

Putting $\lambda=\frac{1}{2}$, $\sigma=\frac{1}{4}$, we obtain

$$\widehat{rr}'=-\frac{P}{2\pi b}u, \quad \widehat{\theta\theta}'=\frac{P}{2\pi b}v, \quad \widehat{r\theta}'=-\frac{P}{2\pi b}w.$$

The numerical values of u, v, w at intervals of 15° in the first quadrant are given in Table V.

χ'' is now determined in the same way as before, *i. e.*, so that it gives $\widehat{rr''}$ and $\widehat{r\theta''}$ with identical values over the right-hand half of the circle, but with negative values over the left-hand half. As in (1.9), we assume

$$u = A_0 + A_2 \cos 2\theta + \ldots + A_{12} \cos 12\theta,$$

$$w = B_2 \sin 2\theta + \ldots + B_{10} \sin \theta,$$

where the A's and B's are given by the same equation (1.10), but the values of u, w are now taken from Table V. Table VI. shows the numerical values of the new coefficients.

TABLE VI.

n.	0.	1.	2.	3.	4.	5.	6.
A_{2n} ...	2·0615	−1·6656	−0·1629	−0·0892	−0·0649	−0·0537	−0·0253
B_{2n} ...	—	0·6835	0·0270	0·0372	0·0273	0·0136	—

The stresses on $\rho = \lambda = \frac{1}{2}$ are now

$$\widehat{rr''} = -\frac{P}{2\pi b} \sum_{n=0}^{6} A_{2n} \cos 2n\theta, \quad \widehat{r\theta''} = -\frac{P}{2\pi b} \sum_{n=1}^{5} B_{2n} \sin 2n\theta. \quad \ldots \quad (2.8)$$

The function χ'' cannot, in this case, be written as in (1.12), for although such a series can be determined to give the required stresses (2.8) on the circle, it would not leave the straight edges of the strip free from stress. To overcome this difficulty we use the alternating approximation process given in " B." We write

$$\chi'' = \chi_0'' + \chi_1'' + \chi_2'' + \ldots, \quad \ldots \quad (2.9)$$

in which χ_0'' gives the required stresses (2.8) on the edges $y = \pm 1$. χ_1'' is a function cancelling these stresses, but giving new stresses on $\rho = \lambda$. These are cancelled by χ_3'', and so on. These functions are determined in the following way. We first assume that the even and odd functions in (2.9) are of the forms

$$\chi_{2r}'' = \frac{Pb}{2\pi} \left[-D_0^{(r)} \log \rho + \sum_{n=1}^{\infty} \left(\frac{D_{2n}^{(r)}}{\rho^{2n}} + \frac{E_{2n}^{(r)}}{\rho^{2n-2}} \right) \cos 2n\theta \right] \quad (2.10)$$

and

$$\chi''_{2r+1} = \frac{Pb}{2\pi}\left[\sum_{n=0}^{\infty}(L^{(r)}_{2n} + M^{(r)}_{2n}\rho^2)\rho^{2n}\cos 2n\theta\right] \quad . \quad . \quad . \quad . \quad (2.11)$$

respectively.

χ_0'' is determined so that it gives the stresses (2.8) on $\rho = \lambda$, and the coefficients in it, $D^{(0)}_0$, etc., will be given by (1.16), (1.17), except that we write $D^{(0)}_0$ for D_0 and use the values of A_{2n}, B_{2n} as given in Table VI. The coefficients in the other χ''_{2r}, χ''_{2r+1} will be given by the recurrence relations of "A," pp. 176–177. These are

$$\left.\begin{aligned} L^{(r)}_{2n} &= {}^{2n}\alpha_0 D^{(r)}_0 + \sum_{p=1}^{\infty}\{{}^{2n}\alpha_{2p} D^{(r)}_{2p} + {}^{2n}\beta_{2p} E^{(r)}_{2p}\}, \\ M^{(r)}_{2n} &= {}^{2n}\gamma_0 D^{(r)}_0 + \sum_{p=1}^{\infty}\{{}^{2n}\gamma_{2p} D^{(r)}_{2p} + {}^{2n}\delta_{2p} E^{(r)}_{2p}\}, \\ D^{(r+1)}_0 &= 2M^{(r)}_0\lambda^2, \\ D^{(r+1)}_{2n} &= \lambda^{4n}\{(2n-1)L^{(r)}_{2n} + 2n\lambda^2 M^{(r)}_{2n}\}, \\ E^{(r+1)}_{2n} &= -\lambda^{4n-2}\{2nL^{(r)}_{2n} + (2n+1)\lambda^2 M^{(r)}_{2n}\}, \end{aligned}\right\} \quad (2.12)$$

where the new coefficients α, β, γ, δ are taken from "A," pp. 178–179. The convergence of this approximation method has been proved by the author in a recent paper *, provided λ is not too large. Comparatively few χ_n'' are necessary to obtain a good approximation. We have, in fact, calculated the coefficients for $n \leq 6$, $r \leq 4$. If we proceed further we shall modify slightly the final coefficients in χ''. These modifications are not important, for the residual stresses on the straight boundaries when we stop at χ_8'' are very small.

If we write

$$\left.\begin{aligned} d_n &= \sum_{r=0}^{4} D^{(r)}_{2n}, \qquad e_{2n} = \sum_{r=0}^{4} E^{(r)}_{2n}, \\ l_{2n} &= \sum_{r=0}^{3} L^{(r)}_{2n}, \qquad m_{2n} = \sum_{r=0}^{3} M^{(r)}_{2n}, \end{aligned}\right\} \quad . \quad . \quad . \quad (2.13)$$

χ'' takes the form

$$\chi'' = \frac{Pb}{2\pi}\left[-d_0\log\rho + \sum_{n=1}^{6}\left(\frac{d_{2n}}{\rho^{2n}} + \frac{e_{2n}}{\rho^{2n-2}}\right)\cos 2n\theta + \sum_{n=0}^{6}(l_2 + m_{2n}\rho^2)\rho^{2n}\cos 2n\theta\right] \quad . \quad (2.14)$$

* Quart. Jour. of Math., Oxford, vol. v. pp. 255–268 (1934).

Table VII. gives the final coefficients in χ''.

TABLE VII.

n.	0.	1.	2.	3.	4.	5.	6.
d_{2n} ...	$5{\cdot}84 \times 10^{-1}$	$4{\cdot}79 \times 10^{-2}$	$9{\cdot}96 \times 10^{-4}$	$5{\cdot}65 \times 10^{-5}$	$5{\cdot}75 \times 10^{-6}$	$7{\cdot}9 \times 10^{-7}$	6×10^{-8}
e_{2n} ...	—	$-4{\cdot}27 \times 10^{-1}$	$-5{\cdot}64 \times 10^{-3}$	$-2{\cdot}84 \times 10^{-4}$	$-2{\cdot}75 \times 10^{-5}$	$-3{\cdot}69 \times 10^{-6}$	$-2{\cdot}8 \times 10^{-7}$
l_{2n} ...	—	$2{\cdot}89 \times 10^{-1}$	$6{\cdot}95 \times 10^{-2}$	$1{\cdot}88 \times 10^{-2}$	$4{\cdot}97 \times 10^{-3}$	$1{\cdot}34 \times 10^{-3}$	$3{\cdot}78 \times 10^{-4}$
m_{2n} ...	$1{\cdot}38 \times 10^{-1}$	$-5{\cdot}69 \times 10^{-2}$	$-3{\cdot}50 \times 10^{-2}$	$-1{\cdot}41 \times 10^{-2}$	$-4{\cdot}92 \times 10^{-3}$	$-1{\cdot}62 \times 10^{-3}$	$-5{\cdot}21 \times 10^{-4}$

We must now examine the infinity conditions as given by the above solution. It is found (see "A," p. 167) that the force P at the origin as given by χ'' is balanced, half by a uniform tension $P/4b$ across the strip at $-\infty$, and half by a uniform pressure $P/4b$ at $-\infty$. This is, then, a possible solution. If, however, we require the force P to be balanced entirely by tensions at $-\infty$ we must superpose a solution for the strip giving a uniform tension $P/4b$ at both $\pm\infty$, while leaving the conditions on the circle and straight edges unchanged. Let χ''' be such a solution, and write

$$\chi=\chi'+\chi''+\chi'''. \quad . \quad . \quad . \quad . \quad . \quad (2.15)$$

Apart from a suitable multiplying factor, actually $\frac{1}{2}$, χ''' is given in "B," pp. 69 *et seq.* We shall not give it in detail here, but later shall use some numerical results for its stresses that appear in "B."

The Rivet in a Strip of Finite Breadth.
Transverse Force.

As in the previous section, we write

$$\chi=\chi'+\chi'',$$

where now χ' corresponds to an isolated force P at the origin acting in direction Oy. It is

$$\chi'=\frac{Pb}{4\pi(1-\sigma)}\Big[(1-2\sigma)\eta\log\rho-2(1-\sigma)\xi\theta + 2\sum_{n=0}^{\infty}({}^{s}a_n+{}^{s}b_n\rho^2)\cos(2n+1)\theta\Big]. \quad (3.1)$$

The coefficients ${}^{\beta}a_n$, ${}^{\beta}b_n$ when $\sigma=0{\cdot}25$ are given in Table VIII.

TABLE VIII.

n.	0.	1.	2.	3.	4.	5.	6.
$\frac{{}^{\beta}a_n}{1-\sigma}\ldots$	0	$-3{\cdot}964\times10^{-1}$	$6{\cdot}002\times10^{-3}$	$-1{\cdot}228\times10^{-3}$	$-2{\cdot}957\times10^{-4}$	$-6{\cdot}311\times10^{-5}$	$-1{\cdot}342\times10^{-5}$
$\frac{{}^{\beta}b_n}{1-\sigma}\ldots$	$1{\cdot}176\times10^{-1}$	$1{\cdot}010\times10^{-1}$	$1{\cdot}529\times10^{-2}$	$3{\cdot}336\times10^{-3}$	$7{\cdot}865\times10^{-4}$	$1{\cdot}902\times10^{-4}$	$4{\cdot}653\times10^{-5}$

The stresses due to χ' when $\rho=\lambda$ are

$$\widehat{rr}' = \frac{P}{2\pi(1-\sigma)b}\sum_{n=0}^{\infty} p_n \cos(2n+1)\theta, \quad . \quad . \quad (3.2)$$

$$\widehat{\theta\theta}' = \frac{P}{2\pi(1-\sigma)b}\sum_{n=0}^{\infty} q_n \cos(2n+1)\theta, \quad . \quad . \quad (3.3)$$

$$\widehat{r\theta}' = \frac{P}{2\pi(1-\sigma)b}\sum_{n=0}^{\infty} r_n \sin(2n+1)\theta. \quad . \quad . \quad (3.4)$$

The coefficients p, q, r are given by equations (2.7), but we now use the values of a_n, b_n as given in Table VIII.

As before, put $\lambda=\frac{1}{2}$, $\sigma=\frac{1}{4}$, and write

$$\widehat{rr}' = -\frac{P}{2\pi b}u, \quad \widehat{\theta\theta}' = \frac{P}{2\pi b}v, \quad \widehat{r\theta}' = -\frac{P}{2\pi b}w.$$

The new values of u, v, w appear in Table IX.

TABLE IX.

$\theta°$.	u.	v.	w.
0	2·1013	0·1249	0
15	2·2282	0·3363	0·4997
30	2·7649	0·8523	0·6281
45	3·0609	1·3206	0·1970
60	2·7567	1·4575	−0·6537
75	1·6597	0·9877	−1·4961
90	0	0	−1·8473

We must now determine χ'' so that it cancels the pressures and shears on the lower half of the circle, *i. e.*, $\pi/2<\theta<3\pi/2$, but doubles them on the upper half. It is clear, however, that it will take the same form as previous χ''s, since it must be even in both x and y. Hence we again assume equations (1.9), (1.10), and obtain the new values of A_{2n}, B_{2n} shown in Table X.

TABLE X.

n.	0.	1.	2.	3.	4.	5.	6.
A_{2n} ...	−2·2535	−0·5157	0·9424	−0·3475	0·1977	−0·1875	0·0628
B_{2n} ...	—	0·1078	−0·9462	0·3978	−0·2061	0·0930	—

The equations (2.8) show the stresses on $\rho=\lambda=\frac{1}{2}$ if the correct values of A_{2n}, B_{2n} are used. The new function χ'' will be determined as in the previous section, and will take the form (2.14). The new coefficients d_n, etc., are tabulated in Table XI.

TABLE XI.

n.	0.	1.	2.	3.	4.	5.	6.
d_{2n} ...	7·15 $\times10^{-1}$	−1·78 $\times10^{-2}$	3·36 $\times10^{-3}$	−2·47 $\times10^{-4}$	2·48 $\times10^{-5}$	−3·32 $\times10^{-6}$	1·5 $\times10^{-7}$
e_{2n} ...	—	1·66 $\times10^{-1}$	−1·79 $\times10^{-2}$	1·18 $\times10^{-3}$	−1·13 $\times10^{-4}$	1·52 $\times10^{-5}$	−7·0 $\times10^{-7}$
l_{2n} ...	—	−2·16 $\times10^{-1}$	−3·79 $\times10^{-2}$	−3·58 $\times10^{-3}$	5·89 $\times10^{-4}$	4·74 $\times10^{-4}$	1·82 $\times10^{-4}$
m_{2n} ...	3·02 $\times10^{-1}$	1·05 $\times10^{-1}$	2·89 $\times10^{-2}$	5·96 $\times10^{-3}$	7·08 $\times10^{-4}$	−1·11 $\times10^{-4}$	−1·15 $\times10^{-4}$

The infinity conditions due to χ' are somewhat different in this case. It has been shown ("A," p. 169) that χ' gives rise to a shear $-\frac{1}{2}P$ at $\pm\infty$ with a bending moment $\frac{1}{2}Px$. There is also a finite bending moment $P/2\pi(1-\sigma)$ at $\pm\infty$. To obtain a further solution we may remove this last quantity by writing

$$\chi=\chi'+\chi''+\chi''',$$

where χ''' corresponds to a stress function giving a finite bending moment $-P/2\pi(1-\sigma)$, while leaving the conditions on the circle and edges unchanged. Such a function has been evaluated in "A," pp. 201 *et seq.*, from which numerical results will be quoted.

The Stresses round the Hole.

The first result which we may obtain, and the one of greatest interest, is the variation of "hoop stress" or tension round the rim of the hole We consider first the infinite plate. Let

$$\widehat{\theta\theta}=\widehat{\theta\theta}'+\widehat{\theta\theta}'', \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.1)$$

where $\widehat{\theta\theta}$ is the stress due to χ and is the sum of the stresses due to the separate χ' and χ''.

The equation (1.7) gives $\theta\theta'$ and Table I. its numerical values at intervals of 15°. For the sake of comparison with later results we tabulate $4a\widehat{\theta\theta}/P$, so that the values already given must be multiplied by a suitable factor. To obtain values outside the range $0<\theta<\pi/2$ we note that $\widehat{\theta\theta}'$ is odd in x but even in y. The contribution of χ'' is found by putting $r'=1$ in (1.14) This leads to an equation of the type

$$\widehat{\theta\theta}''=\frac{P}{a}\sum_{0}^{6} k_{2n}\cos 2n\theta. \quad . \quad . \quad . \quad . \quad (4.2)$$

From this equation we calculate the values of $\widehat{\theta\theta}'$ at intervals of 15°. It has not been thought necessary to tabulate here the values of its coefficients k_{2n}. Table XII. shows the values of the hoop stresses at intervals in the range $-\frac{\pi}{2}<\theta<\pi/2$.

The continuous line in fig. 1 has been drawn from the values of $\widehat{\theta\theta}$ given in Table XII. Positive quantities are measured radially outwards from the circumference, negative quantities radially inwards.

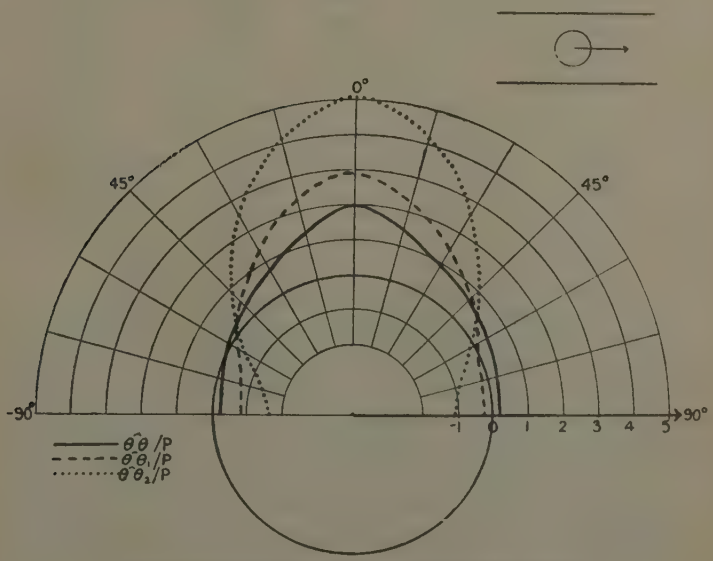
For the longitudinal force in a strip of finite breadth we write

$$\widehat{\theta\theta}_1=\widehat{\theta\theta}'+\widehat{\theta\theta}'' \quad . \quad . \quad . \quad . \quad . \quad (4.3)$$

TABLE XII.

$\theta°$.	$\frac{4a}{P}\widehat{\theta\theta'}$.	$\frac{4a}{P}\widehat{\theta\theta''}$.	$\frac{4a}{P}\widehat{\theta\theta}$.
−90	−·21	·01	−·20
−75	−·20	·07	−·13
−60	−·18	·22	·04
−45	−·15	·50	·35
−30	−·11	·84	·73
−15	−·05	1·40	1·35
0	0	1·97	1·97
15	·05	1·40	1·45
30	·11	·84	·95
45	·15	·50	·65
60	·18	·22	·40
75	·20	·07	·27
90	·21	·01	·22

Fig. 1.



Values of $\widehat{\theta\theta}$/P at edge of hole. Longitudinal force.

when we consider the solution when P is balanced by forces at $\pm\infty$, and

$$\widehat{\theta\theta}_2=\widehat{\theta\theta'}+\widehat{\theta\theta''}+\widehat{\theta\theta'''} \quad . \quad . \quad . \quad . \quad (4.4)$$

when P is balanced by forces at $-\infty$ only.

Equation (2.5) gives $\widehat{\theta\theta'}$ with numerical values from Table V. The contribution of χ'' (equation 2.14) is given by

$$\widehat{\theta\theta''}=\frac{P}{2\pi b}\left\{2m_0+\frac{d_0}{\rho^2}+2\sum_{n=1}^{6}\left(\frac{n(2n+1)d_{2n}}{\rho^{2n+2}}+\frac{(n-1)(2n-1)e_{2n}}{\rho^{2n}}\right.\right.$$
$$\left.\left.+n(2n-1)l_{2n}\rho^{2n-2}+(n+1)(2n+1)m_{2n}\rho^{2n}\right)\cos 2n\theta\right\}. \quad . \quad . \quad . \quad (4.5)$$

TABLE XIII.

$\theta°$.	$\frac{2b}{P}\widehat{\theta\theta'}$.	$\frac{2b}{P}\widehat{\theta\theta''}$.	$\frac{2b}{P}\widehat{\theta\theta'''}$.	$\frac{2b}{P}\widehat{\theta\theta}_1$.	$\frac{2b}{P}\widehat{\theta\theta}_2$.
−90	−·27	−·55	−·79	−·82	−1·61
−75	−·24	−·41	−·66	−·65	−1·31
−60	−·17	−·04	−·25	−·21	− ·46
−45	−·09	·59	·38	·50	·88
−30	−·02	1·41	1·16	1·39	2·55
−15	·01	2·30	1·86	2·31	4·17
0	0	2·87	2·16	2·87	5·03
15	−·01	2·30	1·86	2·29	4·15
30	·02	1·41	1·16	1·43	2·59
45	·09	·59	·38	·68	1·06
60	·17	−·04	−·25	·13	− ·12
75	·24	−·41	−·66	−·17	− ·83
90	·27	−·55	−·79	−·28	−1·07

Putting $\rho=\lambda=\frac{1}{2}$ in this equation, we obtain an equation of type (4.2), from which we calculate the required values of $\widehat{\theta\theta''}$. This completes the determination of $\widehat{\theta\theta}_1$. To obtain $\widehat{\theta\theta}_2$ we add the values of $\widehat{\theta\theta'''}$, which are to be found in "B," p. 74, table xii. They have been multiplied by a suitable constant ($=\frac{1}{2}$).

The calculated values are given in Table XIII., and illustrated by the broken line ($\widehat{\theta\theta}_1$) and the dotted line ($\widehat{\theta\theta}_2$) in fig. 2.

When the rivet is pulled transversely we have again two cases to consider. We write

$$\widehat{\theta\theta}_3=\widehat{\theta\theta'}+\widehat{\theta\theta''} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.6)$$

and

$$\widehat{\theta\theta}_4=\widehat{\theta\theta'}+\widehat{\theta\theta''}+\widehat{\theta\theta'''}. \quad . \quad . \quad . \quad . \quad (4.7)$$

The equation (4.6) gives the stress when we take χ' and χ'' only, while in (4.7) we have added the solution χ''', which corrects the constant bending-moment term at infinity.

TABLE XIV.

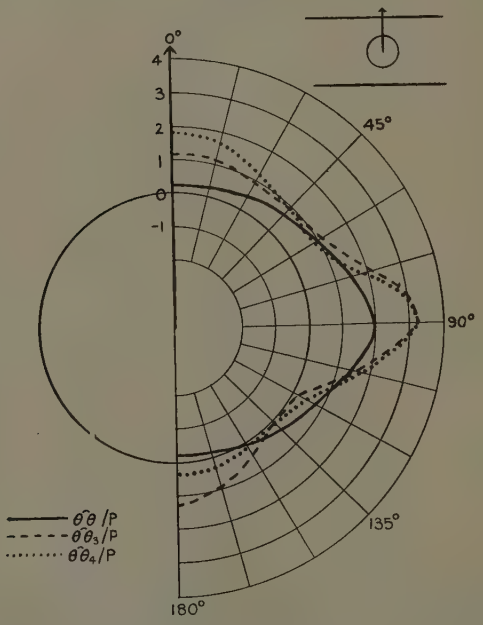
$\theta°$.	$\frac{2b}{P}\widehat{\theta\theta'}$.	$\frac{2b}{P}\widehat{\theta\theta''}$.	$\frac{2b}{P}\widehat{\theta\theta'''}$.	$\frac{2b}{P}\widehat{\theta\theta}_3$.	$\frac{2b}{P}\widehat{\theta\theta}_4$.
0	·04	1·06	·70	1·10	1·80
15	·11	·99	·57	1·10	1·67
30	·27	·64	·27	·91	1·18
45	·42	·47	−·02	·89	·87
60	·46	·61	−·20	1·07	·87
75	·31	1·79	−·16	2·10	1·94
90	0	3·19	0	3·19	3·19
105	−·31	1·79	·16	1·48	1·64
120	−·46	·61	·20	·15	·35
135	−·42	·47	·02	·05	·07
150	−·27	·64	−·27	·37	·10
165	−·11	·99	−·57	·88	·31
180	−·04	1·06	−·70	1·02	·32

$\widehat{\theta\theta'}$ is given by equation (3.3) if the coefficients are taken from Table IX. The contribution of χ'' is obtained from (4.5), with coefficients from Table XI. The extra term in $\theta\theta_4$, *i.e.*, $\widehat{\theta\theta'''}$, has been obtained from table xxi. of paper "A." We have tabulated the values of $2b\widehat{\theta\theta'}/P$, etc., in Table XIV., and these have been plotted in fig. 2. The broken line shows the variation of $\theta\widehat{\theta}_3$ and the dotted line that of $\theta\theta_4$.

It is seen that, in all cases, the maximum value of the tension round the hole occurs at point $\pi/2$ from the line of

action of the force. This value is nearly twice P when the boundaries are at an infinite distance from the hole. When the plate has a finite breadth, and its edges are parallel to the force, this maximum value is increased to three times P when P is balanced by forces at both ends of the strip, and to five times P when the balancing forces are at one end only. Increases of this order were obtained by

Fig. 2.



Values of $\widehat{\theta\theta}$/P at edge of hole. Transverse force.

Howland *, but it has been found that some of his figures given in that paper require slight corrections.

On the line of action of the force in "front" of the hole a slight tension becomes a pressure which is as much as P in the second case. "Behind" the hole a slight pressure is increased up to about $1\frac{1}{2}$P.

* Third Inter. Cong. App. Mech., Stockholm, 1930.

When the edges of the strip are perpendicular to the force the maximum value of the tension is increased in the ratio of about 3 : 2 ; while in the direction of the force small stresses in front and behind become tensions—P and 2P in front, $\frac{1}{2}$P, $1\frac{1}{2}$P behind.

The Stresses in the Direction of the Force.

We shall now investigate the variation of $\widehat{xx}$ in the longitudinal case, along certain lines in the plane.

Firstly, the variation of $\widehat{xx}$ across the minimum section. When $\theta=0$ we have

$$\widehat{xx}_1=\widehat{\theta\theta}_1=\widehat{\theta\theta}'+\widehat{\theta\theta}''.$$

Putting $\theta=0$ in equation (2.5), we see that $\widehat{\theta\theta}'=0$. The second term will be given by (4.4) when $\theta=0$ and $\rho=\eta$. This equation will now give a power series in η from

TABLE XV.

η.	$\frac{2b}{P}\widehat{xx}_1$.	$\frac{2b}{P}\widehat{xx}_2$.	η.	$\frac{4a}{P}\widehat{xx}$.
0·5	2·87	5·03	1·0	1·97
0·6	1·54	2·91	1·2	0·90
0·7	1·00	2·02	1·4	0·56
0·8	0·68	1·48	1·6	0·38
0·9	0·42	1·03	1·8	0·28
1·0	0·32	0·48	2·0	0·21

which we calculate the values of $\widehat{\theta\theta}''$ for $\eta=0{\cdot}5, 0{\cdot}6, \ldots 1{\cdot}0$. Since

$$\widehat{xx}_2=\widehat{xx}_1+\widehat{\theta\theta}''',$$

we obtain its values by adding to $\widehat{xx}_1$ the values given in table xiv. of "B."

For the sake of comparison we evaluate the stresses $\widehat{xx}$ along the same line in the infinite plate. Here we write

$$\widehat{xx}=\widehat{\theta\theta}'+\widehat{\theta\theta}''.$$

As before, $\widehat{\theta\theta}'$ is zero, while the values of $\widehat{\theta\theta}''$ are obtained from equation (1.13) with $\theta=0$, $\rho=\eta$. We must note, however, that η now takes the values 1·0, 1·2, ... 2·0. The three sets of values are tabulated in Table XV. and shown graphically in fig. 3.

We next consider the values of $\widehat{xx}$ on the axis of the strip. The series from which we have to calculate the stresses will be sufficiently rapidly convergent if $|\xi| < 1$, and we shall evaluate $\widehat{xx}$ only within this range. This is quite sufficient for our purpose, as we shall see that there is no great difference between the results in the three cases when we reach the limit of this range.

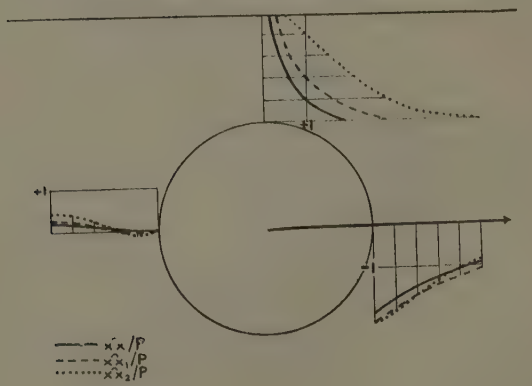
On the axis

$$\theta = \frac{\pi}{2},\ \rho = \xi, \quad \text{or} \quad \theta = -\frac{\pi}{2},\ \rho = -\xi,$$

and

$$\widehat{xx}_1 = \widehat{rr}_1 = \widehat{rr}' + \widehat{rr}''.$$

Fig. 3.



Variation of $\widehat{xx}$.

$\widehat{rr}'$ is given by (2.4), while $\widehat{rr}''$ has the form

$$\widehat{rr}'' = \frac{P}{2\pi b}\left\{2m_0 - \frac{d_0}{\rho^2} + 2\sum_{n=1}^{\infty}\left(\frac{n(2n+1)d_{2n}}{\rho^{2n+2}} + \frac{(n+1)(2n-1)e_{2n}}{\rho^{2n}} + n(2n-1)l_{2n}\rho^{2n-2} + (n-1)(2n+1)m_{2n}\rho^{2n}\right)\cos 2n\theta\right\}. \quad \ldots \quad (1.5)$$

The coefficients in this series are to be taken from Table VII. In (2.4) and (5.1) we must put $\theta = \frac{\pi}{2}$, $\rho = \xi$ to obtain $\widehat{xx}$ in front of the hole, and $\theta = -\frac{\pi}{2}$, $\rho = -\xi$ to obtain $\widehat{xx}$ behind the hole.

The tension $\widehat{xx}_2$ is obtained by the addition of $\widehat{rr'''}$ from table xv. of "B." These results are compared with $\widehat{xx}$ on

TABLE XVI.

ξ.	$-\frac{2b}{P}\widehat{xx}_1$.	$-\frac{2b}{P}\widehat{xx}_2$.	ξ.	$-\frac{4a}{P}\widehat{ww}$.
0·5	2·30	2·30	1·0	2·12
0·6	2·01	2·06	1·2	1·76
0·7	1·72	1·71	1·4	1·48
0·8	1·48	1·40	1·6	1·25
0·9	1·25	1·09	1·8	1·08
1·0	1·13	0·91	2·0	·94

TABLE XVII.

ξ.	$\frac{2b}{P}\widehat{xx}_1$.	$\frac{2b}{P}\widehat{xx}_2$.	ξ.	$\frac{4a}{P}\widehat{xx}$.
−0·5	0	0	−1·0	0
−0·6	−0·03	−0·08	−1·2	0
−0·7	0·02	0·03	−1·4	0·04
−0·8	0·10	0·18	−1·6	0·07
−0·9	0·21	0·37	−1·8	0·10
−1·0	0·23	0·45	−2·0	0·12

the axis, *i. e.*, in the direction of the force, in the infinite plate. These last values are obtained from (1.6) and (1.13). Table XVI. gives the numerical values $\widehat{xx}$ in front of the hole and Table XVII. gives them behind the hole. The three sets of results on both lines are shown in fig. 3.

We notice that there is little difference between the stresses on the axis of the strip. Across the minimum

section the tension is increased near the hole in the ratio of approximately 5 : 2 and 3 : 2. The tension in the edge is not much greater than the tension along that line in the infinite plate; so it appears that when we get away from the hole a distance equal to its radius the effect of the boundaries is negligible.

Finally, we evaluate the stresses $\widehat{yy}$ along the same lines when the force is acting transversely. On the minimum section $\widehat{yy}=\widehat{rr}$, so that

$$\widehat{yy}_3=\widehat{rr}'+\widehat{rr}''$$

when

$$\theta=0,\ \rho=\eta \quad \text{or} \quad \theta=\pi,\ \rho=-\eta.$$

Equation (3.2) gives $\widehat{rr}'$, while $\widehat{rr}''$ is obtained from equation (5.1) but with coefficients d_n, etc., from

TABLE XVIII.

η.	$-\frac{2b}{P}\widehat{yy}_3$.	η.	$\frac{2b}{P}\widehat{yy}_3$.	ξ.	$\frac{2b}{P}\widehat{yy}_3$.
0·5	1·34	−0·5	0	0·5	3·19
0·6	0·77	−0·6	0·07	0·6	1·29
0·7	0·44	−0·7	0·04	0·7	0·75
0·8	0·21	−0·8	0·03	0·8	0·51
0·9	0·07	−0·9	0·01	0·9	0·36
1·0	−0·04	−1·0	−0·02	1·0	0·25

Table XI., putting $\theta=0$ or π and $\rho=\eta$ or $-\eta$. The resulting values are shown in Table XVIII.

$\widehat{yy}_4$, which is obtained from $\widehat{yy}_3$ by adding the stresses due to the bending-moment solution, will not be given here. The required numerical results are not tabulated in "A," and it has not been thought worth while evaluating them. In any case the difference between $\widehat{yy}_4$ and $\widehat{yy}_3$ will not be great.

In order to compare these last results with the corresponding ones for the infinite plate, we require $\widehat{rr}$ in the direction of the force. These values have been found already, and appear as $\widehat{xx}$ in Tables XVI. and XVII.

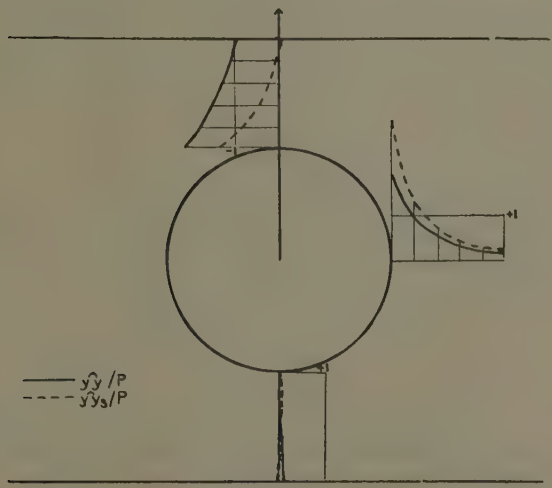
On the axis of the strip

$$\widehat{yy}_3=\widehat{\theta\theta}_3=\widehat{\theta\theta}'+\widehat{\theta\theta}'' \quad \text{when} \quad \theta=\pi/2.$$

$\widehat{\theta\theta'}$ is zero, as is seen from (3.3); while (4.4), with the correct values of d_n, etc., and with $\theta=\pi/2$, $\rho=\xi$, gives the required $\widehat{\theta\theta''}$. For comparison, we require $\widehat{\theta\theta}$ when $\theta=0$. These values are given as $\widehat{xx}$ in Table XV. The variations of $\widehat{yy}$ along the three lines are given numerically in Table XVIII. and shown graphically in fig. 4.

This last set of results shows that again the edges cause little effect on the axis except that the transverse tension is slightly increased. On the minimum section there is a

Fig. 4.



Variation of $\widehat{yy}$.

decrease in pressure of practically a constant amount in front of the hole, but with no appreciable change behind.

The Effect of a Change in σ.

In our calculations we have taken σ to be 0·25. This corresponds to a Poisson's ratio of $\frac{1}{3}$. If this ratio were $\frac{1}{4}$, roughly the value for steel, σ would be 0·2. We shall consider briefly the effect of changing σ from 0·25 to 0·2 in one of the cases that we have taken in this paper, namely, the solution for a finite strip with the rivet

pulled longitudinally and balanced by forces at one end. Here χ is made up of three functions, χ', χ'', χ'''.

χ''' is independent of σ, and contributes about 40 per cent. of the hoop stress at its maximum point. The contribution of χ' is small, and is actually zero when the total stress is greatest. It depends on σ through the values v of Table I. The largest contribution is from χ'', which is calculated from u, w of the same table. Hence it was thought of interest to calculate these values, u, v, w when $\sigma=0{\cdot}2$. This was done, and there was found a decrease of approximately 5 per cent. at the maximum point. It therefore seems that the factor $1/(1-\sigma)$ is of greater importance than the rather complex way in which σ occurs in the coefficients. The change considered would alter this factor by 15/16, which is of the order noted.

The resultant effect in $\widehat{\theta\theta}$ at the maximum point is, therefore, of the order of a decrease of 3 per cent.

In conclusion I should like to thank Professor R. C. J. Howland for suggesting the problem and the helpful advice he has given me during the writing of the paper.

I also gratefully acknowledge the assistance of the Research Committee of University College, Southampton, which made possible the use of a calculating machine.

XLVI. *A General Property of Two-Dimensional Thermal Stress Distribution* *. *By* M. A. Biot, *Harvard University (Cambridge, U.S.A.)* †.

WE consider a two-dimensional temperature distribution in an arbitrary cylindrical body; the temperature is supposed to be the same along any straight line parallel to the generators. We shall also assume that this temperature distribution has reached a state of equilibrium—*i. e.*, the temperature may be different from point to point, but it remains constant at a given point and has any given arbitrary distribution along the boundary of the cross-section (fig. 1).

* See also M. A. Biot, "Propriété générale des tensions thermiques en régime stationnaire dans les corps cylindriques. Application à la mesure photo-elastique de ces tensions," *Ann. de la Soc. Sc. de Bruxelles*, liv. B (janvier 1934).

† Communicated by Prof. R. V. Southwell, M.A., F.R.S.

As we know, such a temperature distribution has the following property: the value of the temperature θ as a function of the coordinates x, y in a cross-sectional plane must satisfy the equation

$$\frac{\partial^2\theta}{\partial x^2}+\frac{\partial^2\theta}{\partial y^2}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

We shall show that, owing to this condition, the stresses which may arise from this temperature distribution exhibit remarkable properties stated by the theorem on p. 547. The theorem may also be applied to an elastic

Fig. 1.

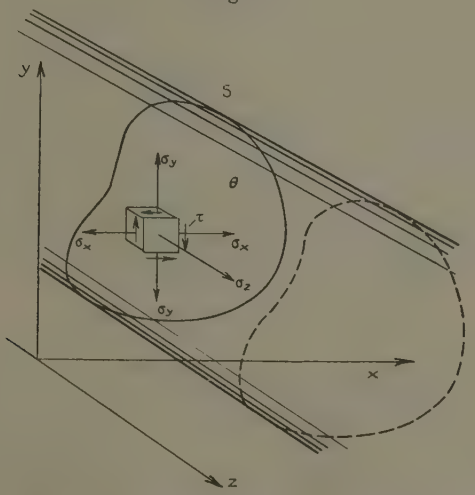


plate for which heat can enter or leave the material only at the boundary. We shall deduce these properties for the case of the cylindrical body: it is easy to see what they become for a plate.

Let us consider a cylindrical elastic body of Young's modulus E and Poisson's ratio ν, the x, y plane being taken along a cross-section (fig. 1). We assume that there is a steady two-dimensional temperature distribution in this cylinder, the same in every cross-section (independent of z), also that the resulting deformation of the cylinder can only be two-dimensional (also independent of z), so that the cross-sections of the cylinder remain parallel

and identical with one another. Calling k the coefficient of thermal expansion, let us put $\epsilon = k\theta$. The thermal extension ϵ varies from point to point: it will not give the actual extensions, since such values would generally not be compatible and would give rise to thermal stresses.

The variables entering the problem must satisfy three groups of equations:—

(1) The equilibrium condition for internal stresses $(\sigma_x\ \sigma_y \tau\ \sigma_z)$:

$$\left.\begin{aligned} \frac{\partial \sigma_x}{\partial x} + \frac{\partial \tau}{\partial y} &= 0, \\ \frac{\partial \tau}{\partial x} + \frac{\partial \sigma_y}{\partial y} &= 0, \\ \frac{\partial \sigma_z}{\partial z} &= 0. \end{aligned}\right\} \quad \ldots\ldots\ (2)$$

(2) The so-called compatibility equation for the strain components $(\epsilon_x\ \epsilon_y\ \gamma)$:

$$\frac{\partial^2 \epsilon_y}{\partial x^2} + \frac{\partial^2 \epsilon_x}{\partial y^2} = \frac{\partial^2 \gamma}{\partial x \partial y}. \quad \ldots\ldots\ (3)$$

(3) The relation between the stress and the strain as a function of the thermal dilatation ϵ:

$$\left.\begin{aligned} \epsilon_x - \epsilon(1+\nu) &= \frac{1}{E}[\sigma_x(1-\nu^2) - \nu(1+\nu)\sigma_y], \\ \epsilon_y - \epsilon(1+\nu) &= \frac{1}{E}[\sigma_y(1-\nu^2) - \nu(1+\nu)\sigma_x], \\ \tau &= 2G\gamma, \\ \sigma_z &= -E\epsilon + \nu(\sigma_x + \sigma_y). \end{aligned}\right\} \quad . \quad (4)$$

From this system we immediately see that the stresses $\sigma_x\ \sigma_y\ \tau$ may disappear under certain conditions. If we put

$$\sigma_x = \sigma_y = \tau = 0,$$

we are left with the conditions

$$\left.\begin{aligned} \sigma_z &= -E\epsilon, \\ \epsilon_x - \epsilon(1+\nu) &= 0, \\ \epsilon_y - \epsilon(1+\nu) &= 0, \\ \gamma &= 0, \\ \frac{\partial^2 \epsilon_y}{\partial x^2} + \frac{\partial^2 \epsilon_x}{\partial y^2} &= \frac{\partial^2 \gamma}{\partial x \partial y}, \end{aligned}\right\} \quad \ldots\ldots\ (5)$$

which, by elimination of ϵ_x ϵ_y, reduce to

$$\sigma_z = -\mathrm{E}\epsilon,$$
$$\frac{\partial^2 \epsilon}{\partial x^2} + \frac{\partial^2 \epsilon}{\partial y^2} = 0.$$

Since $\epsilon = k\theta$ is proportional to the temperature θ, we may also write the condition in the form

$$\sigma_z = -\mathrm{E}\epsilon,$$
$$\frac{\partial^2 \theta}{\partial x^2} + \frac{\partial^2 \theta}{\partial y^2} = 0.$$

Comparing with equation (1), we see that this last condition is automatically satisfied in our case because we assumed the temperature distribution to be steady (independent of the time). Hence this steady state of temperature distribution is a necessary condition for the cancellation of the stresses σ_x, σ_y, τ ; but, as we shall see, it is a sufficient condition only in the case of a solid cylinder. If the cylinder is hollow more conditions have to be satisfied. In order to establish this conclusion let us investigate the problem further.

Consider the strain components given by equation (5)

$$\left.\begin{aligned} \epsilon_x &= \epsilon(1+\nu) = \epsilon', \\ \epsilon_y &= \epsilon(1+\nu) = \epsilon', \\ \gamma &= 0. \end{aligned}\right\} \quad \ldots\ldots \quad (6)$$

Due to the deformation a point of coordinates x, y before deformation becomes of coordinates $x+u$, $y+v$ after deformation ; moreover, each element undergoes a rotation

$$\omega = \frac{1}{2}\left(\frac{\partial v}{\partial x} - \frac{\partial u}{\partial y}\right).$$

By introducing the displacements u, v we may write (6) and ω in the form

$$\left.\begin{aligned} \frac{\partial u}{\partial x} &= \epsilon', \\ \frac{\partial v}{\partial y} &= \epsilon'. \end{aligned}\right\} \quad \ldots\ldots \quad (7)$$

$$\left.\begin{aligned} \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} &= 0, \\ \frac{\partial v}{\partial x} - \frac{\partial u}{\partial y} &= 2\omega. \end{aligned}\right\} \quad \ldots\ldots \quad (8)$$

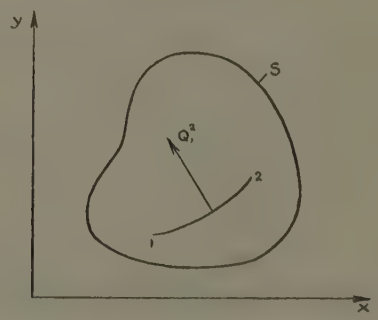
This leads to the relations

$$\left.\begin{aligned} \frac{\partial u}{\partial y} &= -\omega, \\ \frac{\partial v}{\partial x} &= \omega, \end{aligned}\right\} \quad \ldots\ldots \quad (9)$$

$$\left.\begin{aligned} \frac{\partial \epsilon'}{\partial y} &= -\frac{\partial \omega}{\partial x}, \\ \frac{\partial \epsilon'}{\partial x} &= \frac{\partial \omega}{\partial y}, \end{aligned}\right\} \quad \ldots\ldots \quad (10)$$

which show that $Z = \epsilon' + i\omega$ is a complex function of $z = x + yi$. From these results we may calculate the value

Fig. 2.



of the rotation ω and the displacements u, v. The difference of the rotation at point 2 and the rotation at point 1 (fig. 2) is given by the integral

$$\omega_2 - \omega_1 = \int_1^2 \left(\frac{\partial \omega}{\partial x} dx + \frac{\partial \omega}{\partial y} dy \right),$$

which, from relation (10), may be written

$$\omega_2 - \omega_1 = \int_1^2 \left(-\frac{\partial \epsilon'}{\partial y} dx + \frac{\partial \epsilon'}{\partial x} dy \right). \quad \ldots \quad (11)$$

Now since $\left(\frac{\partial \epsilon'}{\partial x}, \frac{\partial \epsilon'}{\partial y} \right)$ is proportional to the temperature gradient, the above difference of rotation $\omega_2 - \omega_1$ is proportional to the amount of heat Q_{12} flowing, parallel

to the cross-section, between the points 1 and 2. We may write

$$\omega_2 - \omega_1 = Q_{12}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

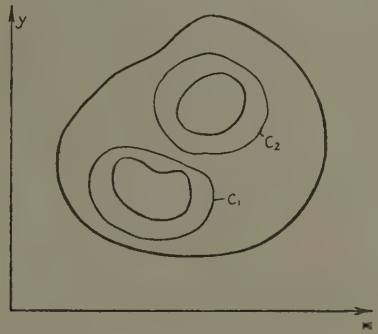
It is easily verified from relations (7) and (9) that the displacement of point 2 relative to point 1 is given by

$$u_2 - u_1 + i(v_2 - v_1) = \int_1^2 \left\{ \frac{\partial u}{\partial x} dx + \frac{\partial u}{\partial y} dy + i \left(\frac{\partial v}{\partial x} dx + \frac{\partial v}{\partial y} dy \right) \right\}$$

$$= \int_1^2 (\epsilon' + i\omega)(dx + i\, dy) = \int_1^2 Z(z) dz. \quad . \quad (13)$$

Now the condition $\sigma_x = \sigma_y = \tau = 0$ for the stresses will be satisfied only if the values of the rotation and the

Fig. 3.



displacements calculated from the above formula and corresponding to such a condition have a physical meaning.

Consider first a solid cylinder, no heat source being present inside; then the functions ϵ' and ω have no singularities inside any closed contour drawn on the area of the cross-section; therefore in this case the rotation and the displacements are single-valued, they have a physical meaning and actually exist. Hence in the case of a solid cylinder under the above condition of heat-flow the stresses σ_x, σ_y, τ actually disappear.

For a hollow cylinder, however (cross-section fig. 3), due to the fact that the holes may contain heat sources or any other kind of singularity of the function Z, we have to complete the previous result. If we take any closed contour C around a hole, the rotation ω given by integral

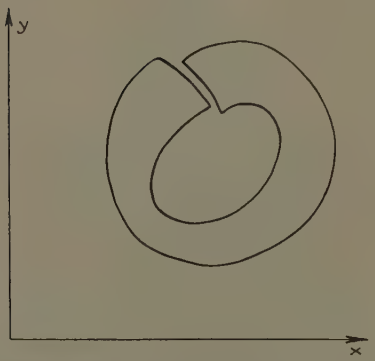
(11) has to be single-valued. From considerations above (12) this means that the total amount of heat flowing out of each hole must be zero. Moreover, the displacements (13) along the same contour must also be single-valued, and this introduces another condition for the following integral taken around each hole:

$$\int_{C_i} (\epsilon' + i\omega) dz = 0,$$

or

$$\left.\begin{aligned} \int_{C_i} (\epsilon' dx - \omega\, dy) &= 0, \\ \int_{C_i} (\omega\, dx + \epsilon'\, dy) &= 0. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Fig. 4.



For a hollow cylinder, if the last conditions are not satisfied, the values of the rotation and the displacements may not be single-valued; this means physically that the stresses thus produced are of the "dislocation" type. Consider, for instance, a cylinder with a cross-section having only a single hole. Let us cut this cylinder by a cylindrical slit (cross-section fig. 4), so as to connect the inside with the outside and transform it into a simply connected body. If then the temperature distribution is stationary and two-dimensional, as already mentioned, the two sides of the slit will either stick together without any relative motion or they will separate. This separation will occur whenever the total amount of heat flowing

from the inside to the outside is not zero and whenever the conditions (14) are not satisfied. Due to the presence of the slit the cylinder behaves like a solid one without holes, and the stresses σ_x, σ_y, τ are zero. If we bring together the two sides of the slit we produce stresses of a dislocation type.

Hence we may finally state the following theorem :—

If a solid cylinder is heated either uniformly or not, but in such a way that a steady-state temperature distribution exists the same in every cross-section, the only stress produced is a tension (or compression) σ_z, acting normally to the cross-section and equal to $\sigma_z = -\mathrm{E}\epsilon = -\mathrm{E}k\theta$, where E is Young's modulus for the cylinder, k its coefficient of thermal expansion, and θ the temperature.

We may say that in such a case *the cylinder expands freely in the plane of its cross-section.*

The same theorem holds for a hollow cylinder provided :

(1) *The total amount of heat flowing in or out each hole is zero.*

(2) *The following contour integrals around each hole are zero* :

$$\int_C (\epsilon' dx - \omega\, dy) = 0,$$

$$\int_C (\omega\, dx + \epsilon' dy) = 0.$$

Applications.

(1) *Circular Tube.*

A circular tube filled with a hot liquid sends out a radial symmetrical flow of heat. The function $\mathrm{Z} = \epsilon + i\omega$ corresponding with this temperature distribution can be written, taking the centre of the tube as origin, as

$$\mathrm{Z} = \mathrm{A} \log z.$$

If we cut a radial slit, the two edges have a relative motion (u, v) given by

$$u + iv = \int_C \mathrm{A} \log z\, dz = [\mathrm{A}z \log z]_C = 2\pi i \mathrm{A}(x + yi),$$

where x, y are the coordinates of a point along the slit. We see that the relative displacement of the two sides of a radial slit is a rotation around the axis of the tube (fig. 5). The stresses in the circular tube are the same as

those produced in the slitted tube by bringing the two sides of the slit together again ; this coincides with the problem of bending of a curved beam.

Fig. 5.

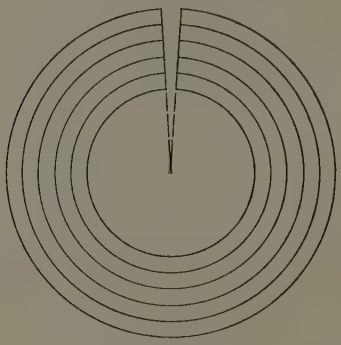
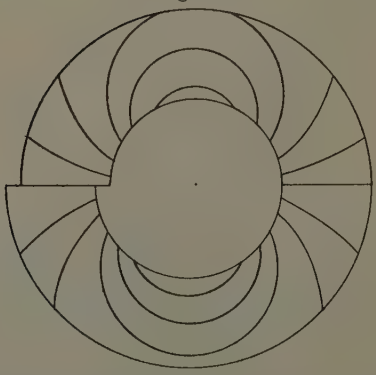


Fig. 6.



If the temperature distribution in the cylinder is such that Z can be represented by

$$Z = \frac{A}{z},$$

it is easily seen that this corresponds with the case of a slit of which the two sides do not separate but simply glide over one another. The isothermal lines are arcs of circles (fig. 6).

Finally, a temperature distribution which can be represented as

$$Z = \frac{A_2}{z^2} + \frac{A_3}{z^3} + \cdots \frac{A_n}{z^n} + \cdots$$

does not produce any dislocation at the slit, hence does not produce any stress σ_x, σ_y, τ.

(2) If a hollow cylinder of arbitrary shape has no heat source inside the holes, and exhibits a two-dimensional steady-state temperature distribution the same in every cross-section, the stresses σ_x, σ_y, τ may be different from zero; but if we fill up the holes with a liquid of same thermal conductivity as that of the material of the cylinder, those stresses disappear, owing to the fact that the function Z cannot have any more singularities inside the holes, and the contour integrals become zero.

(3) *Thermal Stresses measured by Photo-elasticity.*

The identification of the thermal stress problem in a case of steady heat flow with a dislocation problem makes possible the investigation of those thermal stresses by photo-elasticity. All we have to do is to cut a slit in the photo-elastic model and separate the sides of that slit in such a way that the relative displacement of those sides is the same as it would be if due to the given temperature distribution.

XLVII. *The Nuclear Structure of Beryllium and the Mass of the Neutron.* *By* HAROLD J. WALKE, *M.Sc., A.Inst.P., Demonstrator in Physics, Washington Singer Laboratories, University College, Exeter* *.

I. *Introduction.*

THE fact that there is no emission of either protons or neutrons from helium, carbon, and oxygen when bombarded by high-speed ions seems to confirm Rutherford's original suggestion that the nuclei of these elements consist of α-particles, and the stability of the nuclei He_2^4, C_6^{12}, and O_8^{16} is also suggested from mass spectrography, as the curve showing the relation between

* Communicated by Prof. F. H. Newman, D.Sc.

packing fraction and mass number for helium, carbon, and oxygen lies well below that for the other light elements, and these two curves indicate that the elements of odd atomic number consist of less tightly bound components than these stable nuclei. Since α-particles have been ejected from carbon and oxygen when bombarded by neutrons it appears that these nuclei consist of close combinations of α-particles, and the spontaneous ejection of α-particles from radioactive elements (together with the fine structure effects and γ-radiation) suggests that the α-particle is a stable nuclear unit and that it exists within the nucleus as an α-particle.

It has therefore been suggested * that nuclei are built up of the maximum number of α-particles, and if of odd atomic number a diplon and neutrons. According to this scheme the isotopes of beryllium of mass numbers 8 and 9 consist of two α-particles and two α-particles and a neutron respectively. Bainbridge †, however, has measured the mass of the heavier isotope by means of his mass spectrograph, and in view of the high value obtained, namely $9{\cdot}0155 \pm 0{\cdot}0008$, he has concluded that the nuclear structure is not as suggested, since the mass of this nucleus is greater than the sum of the masses of two α-particles, and the accepted value of the mass of the neutron 1·0067. Thus, if He_2^4, C_6^{12}, and O_8^{16} consist of one, three, and four α-particles respectively, Be_4^8 does not contain two α-particles. As the mass of the α-particle is known accurately, the neutron mass is the quantity which has caused Bainbridge to reject $2\alpha+n$ as the nuclear structure of Be_4^9. Hence either the nuclear structure of beryllium is different, as suggested by Bainbridge, or the mass of the neutron is greater than at present determined.

It is the purpose of the present paper to consider the nuclear structure of beryllium in relation to the disintegration experiments in which the light elements have been bombarded with various particles.

II. *The Disintegration of Lithium.*

On the scheme of nuclear structure suggested in a previous paper‡ the lithium isotopes of mass numbers

* Walke, Phil. Mag. xvii. p. 793 (1934).
† Bainbridge, Phys. Rev. xliii. p. 103 (1933).
‡ Walke, *loc. cit.*

6 and 7 consist of an α-particle and a diplon, Li_3^6, and an α-particle, a diplon, and a loosely bound neutron, Li_3^7. The ejection of neutrons when lithium is bombarded with α-particles is thus due to the following reaction :—

$$Li_3^7 \quad \{[\alpha]+(\overline{p+n}+n)\}+\alpha \rightarrow B_5^{10}\{[2\alpha]+(\overline{p+n})\}+\overset{\nearrow}{n}.$$

Thus the newly formed boron nucleus contains two α-particles, and this is confirmed from the disintegration of boron by various ions.

In addition, when lithium is bombarded with protons or diplons the following actions have been observed :

$$Li_3^7 \quad \{[\alpha]+(\overline{p+n}+n)\}+p \rightarrow \overset{\nearrow}{\alpha}+\overset{\nearrow}{\alpha},$$

$$*Li_3^7 \quad \{[\alpha]+(\overline{p+n}+n)\}+p \rightarrow \overset{\nearrow}{\alpha}+\overset{\nearrow}{He_2^3}+\overset{\nearrow}{n},$$

$$Li_3^5 \quad \{[\alpha]+(\overline{p+n})\}+p \rightarrow \overset{\nearrow}{\alpha}+He_2^3,$$

$$Li_3^7 \quad \{[\alpha]+(\overline{p+n}+n)\}+\overline{p+n} \rightarrow \overset{\nearrow}{\alpha}+\overset{\nearrow}{\alpha}+\overset{\nearrow}{n},$$

$$Li_3^8 \quad \{[\alpha]+(\overline{p+n})\}+\overline{p+n} \rightarrow \overset{\nearrow}{\alpha}+\overset{\nearrow}{\alpha},$$

$$Li_3^6 \quad \{[\alpha]+(p+n)\}+\overline{p+n} \rightarrow,$$

$$Li_3^7 \quad \{[\alpha]+(\overline{p+n}+n)\}+\overset{\nearrow}{p},$$

and confirm the suggested structure of the lithium isotopes, the new α-particle being formed by the union of the bombarding particles with the loosely bound components of these nuclei. This α-particle and the single α-particle forming the nuclear core are ejected, because the nuclei Be_4^8 or Be_4^9 are produced with excess energy and disintegrate, the excess energy being emitted as kinetic energy of the α-particles. It may be objected on this account that these nuclei are complexes with excess energy which disintegrate in order that the emitted particles shall carry away the excess energy; but, on the other hand, the way in which these nuclei split up in these transmutations shows how the components are arranged within these nuclei. Moreover, the second reaction † suggests very definitely the formation of

* See, however, note at end of paper.

† See note at end of paper.

a new α-particle in a state of excess energy which disintegrates into He_2^3 and a neutron, as observed by Oliphant and Harteck.

III. *The Disintegration of Boron.*

In a similar manner the disintegration of boron when bombarded by protons and diplons indicates that the boron isotopes have the nuclear structure already suggested *, namely, a core consisting of two α-particles and a less tightly bound structure outside the core, this structure consisting of a diplon in the nucleus of B_5^{10} and a diplon plus a loosely bound neutron in that of B_5^{11}.

The following reactions suggest this structure :—

$$B_6^{11} \quad \{[2\alpha]+(\overline{p+n+n})\}+p \rightarrow \overset{\nearrow}{\alpha}+\overset{\nearrow}{\alpha}+\overset{\nearrow}{\alpha},$$

$$B_6^{10} \quad \{[2\alpha]+(p+n)\}+p+n \rightarrow \overset{\nearrow}{\alpha}+\overset{\nearrow}{\alpha}+\overset{\nearrow}{\alpha}.$$

In each case the energy set free in the formation of the new α-particle is sufficient to disrupt the core consisting of two α-particles. Thus the two α-particle group (Be_4^8) is apparently stable in these nuclei, but disintegrates into two α-particles on account of the energy released by the reaction.

This experimental evidence confirms the hypothesis that the lithium nuclei are built up on the α-particle core and that the boron nuclei are built up on a core of two α-particles. From the structure of these nuclei it follows that beryllium 8 consists of two α-particles and beryllium of two α-particles plus a loosely bound neutron. This theory is strengthened when we consider the disintegration of oxygen, carbon, and beryllium itself.

IV. *The Disintegration of Oxygen, Carbon, and Beryllium.*

Oxygen and carbon are only broken up by neutrons, α-particles being emitted, as the formation of radio-nitrogen when carbon is bombarded by diplons corresponds to the capture of a proton and not to the disintegration of the carbon nucleus.

* Walke, *loc. cit.*

The reactions are as follows :—

$$C_6^{12} \quad \{[3\alpha]\}+n \rightarrow Be_4^9\{[2\alpha]+(n)\}+\overset{\nearrow}{\alpha},$$

$$O_8^{16} \quad \{[4\alpha]\}+n \rightarrow C_6^{12}\{[3\alpha]+(n)\}+\overset{\nearrow}{\alpha},$$

$$C_6^{12} \quad \{[3\alpha]\}+\overline{\overline{p+n}} \rightarrow N_7^{13}\{[3\alpha]+\overset{*}{p}\}+\overset{\nearrow}{n}.$$

The ejection of an α-particle from oxygen leaving the heavier carbon isotope indicates that oxygen O_8^{16} contains one more nuclear α-particle than C_6^{12}, since the C_6^{13} nucleus consists of C_6^{12} plus a loosely bound neutron. The suggested structure is supported by the experiments of Cockroft and Walton *, who have shown that this nucleus may be formed by bombarding C_6^{12} with diplons, the neutron capture being accompanied by proton emission as follows :—

$$C_6^{12} \quad \{[3\alpha]\}+p+n \rightarrow C_6^{13}\{[3\alpha]+(n)\}+\overset{\nearrow}{p}.$$

The disintegration of the C_6^{12} nucleus with α-particle emission and neutron capture would thus indicate that Be_4^9 consists of two α-particles plus a neutron, and this structure is also indicated by the disintegration of beryllium, as shown later.

Since C_6^{12} apparently consists of three α-particles the formation of C_6^{12} from beryllium by bombardment with α-particles according to the reaction

$$Be_4^9 \quad \{[2\alpha]+(n)\}+\alpha \rightarrow C_6^{12}\{[3\alpha]\}+\overset{\nearrow}{n}$$

involves both the formation of an α-particle within the C_6^{12} nucleus and the capture of the incident particle if Be_4^9 has not itself the nuclear structure indicated. In addition, if beryllium is not constructed as suggested it is difficult to understand why only neutrons are emitted, and these at such low energies of the incident α-particles (Crane, Lauritsen, and Soltan† have observed the emission of neutrons from beryllium under bombardment by α-particles of energy 50,000 e.v.), since if this nucleus consists of some combination of neutrons and protons only it would be anticipated that protons would also

* Cockroft and Walton, Proc. Roy. Soc. A, cxliv. p. 704 (1934).
† Crane, Lauritsen, and Soltan, Phys. Rev. xliv. p. 514 (1933).

be emitted. But the failure to observe proton emission and the ejection of neutrons at all energies of the bombarding particles indicates that one neutron is loosely bound within the nucleus (probably with almost zero binding energy). Also the fact that no other particles have been observed suggests that the remaining structure (virtually corresponding to Be_4^8) is more tightly bound.

In addition, Lewis, Livingston, and Lawrence* observed α-particles of identical range (3·3 cm.) when they bombarded beryllium with protons or diplons, and they interpreted these results as indicating that the bombarding particles merely cause the disintegration of the unstable Be_4^9 nucleus. This would indicate that the normal Be_4^9 nucleus is stable, but that the two α-particles are loosely bound, so that the impact of comparatively low energy particles is sufficient to cause the nucleus to break up into its components. It thus appears that Be_4^8 and Be_4^9 are stable, but only just stable, configurations, consisting of two α-particles and two α-particles and a neutron respectively.

In addition, under bombardment by diplons beryllium has been observed to emit neutrons † according to the reaction

$$Be_4^9 \quad \{[2\alpha]+(n)\}+\overline{p+n}\rightarrow B_5^{10}\{[2\alpha]+(p+n)\}+\overset{\nearrow}{n},$$

and, as it has already been shown that the disintegration experiments indicate that B_5^{10} has the structure suggested, the above reaction is additional evidence supporting the suggested structure of Be_4^9.

It is thus evident that the transmutation experiments favour the nuclear scheme discussed for beryllium, and it is therefore necessary to consider the conflicting evidence from nuclear disintegration and from the mass spectrograph.

V. *The Mass of the Neutron and the Relationship between* He_2^5 *and* Be_4^9.

On account of the first value obtained by Chadwick for the mass of the neutron, namely, 1·0067, it was concluded that the neutron was a close combination of a

* Lewis, Livingston, and Lawrence, Phys. Rev. xliv. p. 55 (1933).

† Livingston, Henderson, and Lawrence, Phys. Rev. xliv. p. 782 (1933).

proton (regarded as the elementary unit of mass) and an electron; but, as Chadwick himself suggested *, such a structure introduces difficulties in connexion with the considerations of the spins of the light nuclei, and he concluded that it was only possible to understand the statistics and spins of the light nuclei if it was assumed that the neutron was a simple particle.

In addition the induced positron radioactivity suggests that the proton consists of a combination of a positron and a neutron, the radioactivity of the "free" proton † being due to the transformation of a proton into a neutron by the emission of a positive electron. β-radioactivity then consists in the transformation of a neutron into a proton, due to a neutron capturing a positive electron of an electron pair ‡ formed within the nucleus.

Auger § has also shown that the γ-radiation observed when paraffin was bombarded by neutrons could be explained if the proton consisted of such a combination of a neutron and positive electron with a mass defect energy of $2\text{–}4\times10^6$ e.v., the mass of the neutron being 1·009–1·011 values, which he obtained from the results of disintegration experiments performed by Curie and Joliot. Thus it appears that the neutron is an elementary particle, the proton being complex, consisting of a positron united with a neutron. The stability of the proton requires that the combination has a mass defect energy, and thus the mass of the neutron may be greater than the value generally accepted. This is confirmed by the recent preliminary experiments of Chadwick and Goldhaber ||, who have concluded that the mass of the neutron is 1·008.

A proton when united with a negative electron would produce a neutron—the two electrons being annihilated in the form of γ-radiation, the neutron remaining.

The apparently conflicting evidence as to the nuclear structure of beryllium may therefore be unreal (especially as Chadwick and Goldhaber || state that mass spectrograph values may be in error by 0·001 unit), as the neutron may be heavier than suggested, the beryllium isotopes

* Bakerian Lecture, 1933.
† Walke, Phil. Mag. xviii. p. 154 (1934).
‡ Walke, Phil. Mag. xvii. p. 1176 (1934).
§ Auger, *Comptes Rendus*, cxcviii. p. 365 (1934).
|| Chadwick and Goldhaber, 'Nature,' cxxxiv. p. 237 (1934).

being just stable, with nearly zero binding energy of the constituent particles; so that if we accept the structure indicated by the transmutation experiments, and assumed that Be_4^8 and Be_4^9 have small binding energies, then the mass of the neutron is apparently

$$9{\cdot}0155-2\times(4{\cdot}00216)=1{\cdot}01118,$$

a value which is slightly greater than suggested by Auger and corresponding to a mass defect of the proton of about 5×10^6 e.v.

In addition, if these nuclei, as suggested, are only just stable the mass of Be_4^8 should be very slightly less than twice the mass of an α-particle, *i. e.*, 8·00432.

The nuclear structure and neutron emission of beryllium under bombardment by low-energy α-particles, and the value of the mass of the neutron suggested above, is probably related to the small abundance (and therefore relative instability) of He_2^5, a helium isotope which is almost certainly just stable but which has not yet been detected. Be_4^9 might be considered as a combination of He_2^4 and He_2^5, He_2^5 consisting of an α-particle and a loosely bound neutron. This structure is confirmed by the action

$$Li_3^7 \quad \{[\alpha]+(\overline{p+n}+n)\}+\overline{p+n}\rightarrow\overset{\nearrow}{\alpha}+\overset{\nearrow}{\alpha}+n,$$

for if He_2^5 were very stable it is probable that no neutrons would be observed, the nuclear core of one α-particle and He_2^5 being ejected in opposite directions. The emission of neutrons by this action therefore suggests that He_2^5 consists of an α-particle with a loosely bound neutron.

If this nucleus consists of such a combination, the binding energy of the neutron being probably very small, the mass of this isotope may be as high as

$$9{\cdot}0155-4{\cdot}00216=5{\cdot}01334.$$

Although this isotope has not been observed experimentally it might be produced artificially by bombarding helium with diplons. If neutrons were emitted Li_3^5 would be produced by proton capture; if protons were emitted He_2^5 would be formed. Li_3^5, containing a "free" proton, is radioactive, and emits positive electrons, so that He_2^5 would be formed. This helium nucleus could thus be produced artificially by nuclear transmutations.

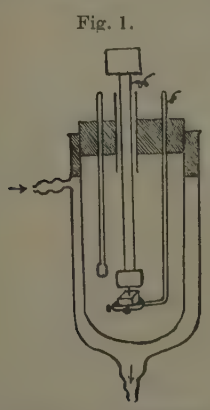
Note.—This reaction, suggested by Oliphant and Rutherford * and discussed by Crane and Lauritsen †, was originally put forward to explain the production of neutrons from lithium bombarded with protons. It does not receive support from the more recent work of Oliphant, Shire, and Crowther.

XLVIII. *The Effect of Heat, Ultra-violet Light, and X-rays on Crystal Rectification.* *By* S. R. Khastgir, *D.Sc.* (*Edin.*), *Reader in Physics, Dacca University, and* Anil Kumar Das Gupta, *M.Sc., Dacca University* ‡.

1. *Introduction.*

FLOWERS § observed a decrease in the rectifying action of galena on heating. When the temperature was raised to 200–300° C. the rectification was

Fig. 1.



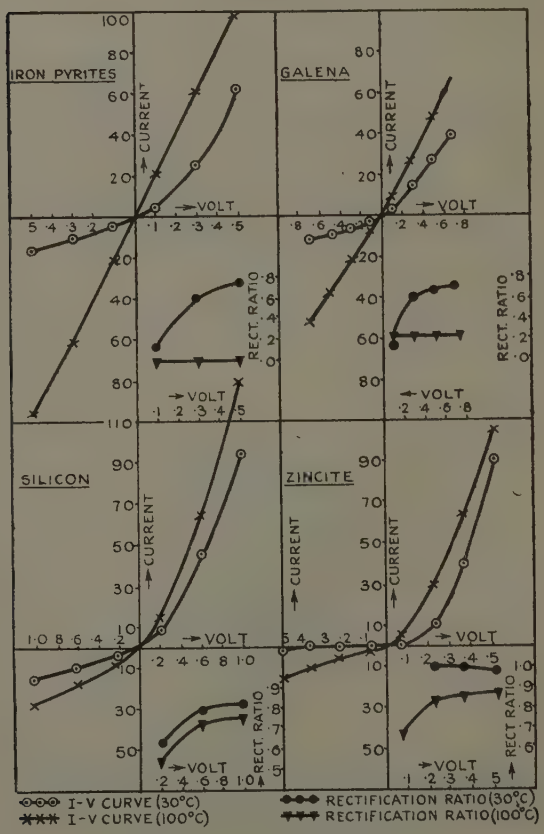
Mounting of the crystal and the whisker to study the effect of heat on rectification.

found to become unstable or disappeared altogether. Experiments by Jackson ‖ showed similar effects when several commercial crystals were exposed to ultra-violet

* Oliphant and Rutherford, Proc. Roy. Soc. A, cxli. p. 259 (1933).
† Crane and Lauritsen, Phys. Rev. xliv. p. 783 (1933).
‡ Communicated by the Authors.
§ Flowers, Phys. Rev. 1909.
‖ Jackson, Phil. Mag., May 1929.

light and X-rays. The rectification effect was found to decrease considerably in many cases. We present in this paper the results of our investigations on the effect of

Fig. 2.



Effect of heat on rectification.

heat, ultra-violet light, and X-rays on the rectifying action of a number of crystals. Some additional knowledge has been gained on the subject which will be of value in any attempt to explain the action of crystal detectors.

2. *Effect of heating the Crystal.*

Each of the crystals under examination was mounted as shown in fig. 1. The whisker, which was a silver pin, was fixed at the end of a weighted brass rod which could slide up and down vertically through a glass tube which passed through a rubber stopper fitting into the mouth of a wide test-tube. The metal ring to which the crystal

TABLE I.

Effect of Heating Crystals.

Applied voltage (volts).	Room-temperature 30° C. (nearly).			100° C.		
	(Galv. scale divs.)		Rectification ratio.	(Galv. scale divs.)		Rectification ratio.
	I_1.	I_2.		I_1.	I_2.	
I. Iron pyrites–Ag :						
·1	4	3·5	·13	21	21	0
·3	25	10	·6	61	61	0
·5	62	16	·74	98	98	0
II. Galena–Cu :						
·1	3	2·5	·17	9	7	·22
·3	15	6	·6	27	21	·22
·5	27	9	·67	48	36	·25
·7	39	11	·72	68	52	·24
III. Silicon–Ag :						
·2	3	9	·67	6	14	·57
·6	9	46	·8	17	65·5	·74
1·0	15	93	·84	27	130	·79
IV. Zincite–Ag ,						
·075	0	0	—	5	2	·67
·225	10	0	1	30	5	·83
·375	40	0	1	65	10	·85
·525	90	2	·98	105	15	·86

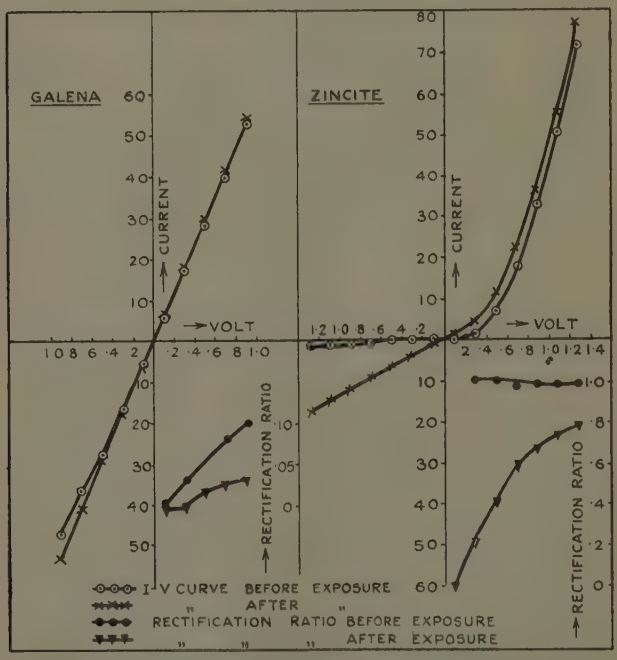
N.B.—I_1 = current from the "whisker" to the crystal, I_2 = corresponding current in the opposite direction. Rectification ratio is taken as the ratio of the difference of the currents in the two opposite directions to the larger value of the current. In the experiments, the results of which are recorded in this paper, the silicon and carborundum crystals showed positive rectification *i. e.*, the current from the crystal to the "whisker" is greater than the corresponding current in the opposite direction. The rest of the crystals mentioned in the paper showed negative rectification.

was fixed was held in position by another brass rod which passed vertically through the rubber stopper. The test-tube, with all the fittings, was enclosed in a wider glass tube. Into the space between the tubes near the mouths

was fitted very tightly an annular cork. There were inlet and outlet tubes for steam in the outer glass tube.

All the crystals (iron pyrites, galena, magnetite, pyrolusite, silicon, zincite, and carborundum) showed a definite decrease in rectification when the temperature was raised to about 100° C. Iron pyrites completely lost

Fig. 3.



Effect of ultra-violet light on rectification.

its power to rectify. Some of the typical results are illustrated in fig. 2. The experimental results are given in Table I.

3. *Effect of Ultra-Violet Light.*

The unfiltered light from a quartz mercury lamp enclosed in a light-tight box passed through an opening, and was allowed to fall directly on to the crystal. The

crystal was fixed in a copper holder, and a silver point was pressed by a spring against the crystal. No filter was used to cut out the heat rays, but the crystal was placed at some distance from the mercury lamp, so that the temperature near the crystal rose only by about 3 or 4° C. on exposure to the light from the mercury lamp. The decrease in rectification observed was extremely small. When, however, the crystal was brought very near the

TABLE II.

Effect of Ultra-violet Light.

Voltage (volts).	Ultra-violet light off. (Galv. scale divs.) I_1.	I_2.	Rectification ratio.	Ultra-violet light on. (Galv. scale divs.) I_1.	I_2.	Rectification ratio.
I. Galena–Ag.:						
·1	5·5	5·5	0	6	6	0
·3	17·0	16·5	·03	17·5	17·5	0
·5	28·0	27·5	·02 ?	29·5	29	·017
·7	39·5	36·5	·08	41·5	40·5	·024
·9	52·5	47	·10	54	52·5	·03
II. Zincite–Cu:						
·1	0	0	—	1	1	0
·3	1·5	0	1·0	4·5	3·5	·22
·5	7	0	1·0	11	6·5	·41
·7	17·5	·5	·97	22	9	·60
·9	32·5	·7	·98	36·5	12	·67
1·1	50	1	·98	55	15	·73
1·3	71	1	·985	77	17·5	·77

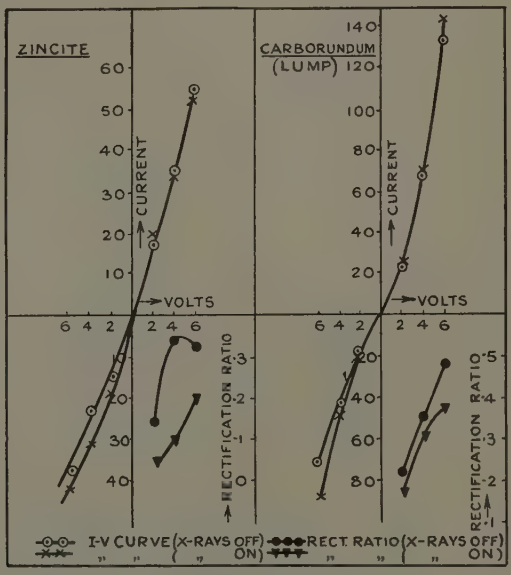
mercury lamp, the decrease was very perceptible. Two typical current-voltage characteristic curves for galena and zincite before and after exposure are shown in fig. 3. (For experimental results see Table II.) The rise of temperature in the neighbourhood of the crystal was as much as 10° C. We therefore attribute this decrease in rectification, partly at any rate, to the heating effect of the crystals.

It is very likely that the marked decrease in rectification on exposure to ultra-violet light observed by Jackson included this heating effect. There is, however, no record in his paper of any rise of temperature in the neighbourhood of the crystal.

4. *Effect of X-Rays.*

Copper K radiation from a Hadding tube working at a peak-voltage of 45 kv. was employed in investigating the effect of X-rays on the rectifying action of crystals. As the experiments of Oberto * showed that the effect of X-rays could be traced to the coherer action produced by spark-discharges, the transformer and the X-ray tube in our experiments had been kept

Fig. 4.



Effect of X-rays on rectification.

running throughout the time during which the two sets of experiments were made, one with the lead shutter on and the other with the shutter off to let out the narrow beam of X-rays. All the crystals examined (iron pyrites, galena, carborundum, zincite, and silicon) showed a distinct decrease in rectification on exposure. This was tested, in the case of iron pyrites and galena, by direct experiments with 1000 cycles/sec. A.C. The rectifying

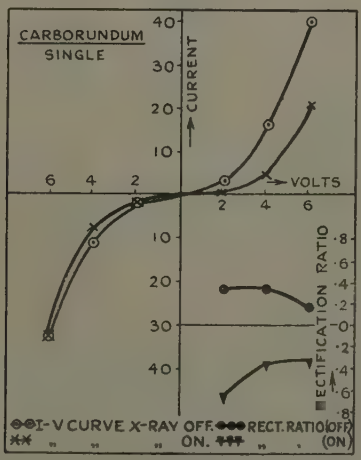
* A summary of his paper is given in 'Nature,' cxxiv. (30th Nov., 1929).

TABLE III.

Effect of X-rays.

Voltage (volts).	X-rays off. (Galv. scale divs.) I_1.	I_2.	Rectification ratio.	X-rays on. (Galv. scale divs.) I_1.	I_2.	Rectification ratio.
I. Zincite–Ag :						
2	17·5	15	·14	20	19	·05
4	35	23	·34	34	31	·25
6	55	37	·33	52	42	·20
II. Carborundum–Ag (lump crystal) :						
2	18	23	·22	20	24	·17
4	43	66	·35	48	70	·31
6	70	134	·48	90	144	·37
III. Carborundum–Ag (single crystal) :						
2	2	3	·33	1·5	·5	−·67
4	11	16·5	·33	8	5	−·38
6	33	40	·17	33	21	−·36

Fig. 5.



Change in the sign of rectification on exposure to X-rays.

power was practically lost in these crystals. In the other cases, besides these direct experiments, a definite flatness in the slope of the current-voltage characteristic

curve indicated the decrease in the rectification. The decrease in the case of silicon was comparatively small. Fig. 4 illustrates the decrease in the rectifying action of zincite and carborundum on exposure to X-rays. Table III. gives the experimental results. The change was effected in less than 10 minutes' time, after which a steady state was attained. The change persisted for several hours after the X-rays were withdrawn.

In some cases carborundum showed an unmistakable change in the sign of the rectification effect. Typical current-voltage characteristic curves with X-rays off and on are shown in fig. 5 to illustrate the change in the sign. The actual experimental results are incorporated in Table III. Direct test with 1000 cycles/sec. A.C. also showed very effectively this change in the sign of the rectification effect.

Of all the crystals employed in this investigation carborundum was the only one which approximated a single crystal. The iron pyrites crystal had also a good crystalline form. The rest had irregular forms.

5. *Conclusions.*

We do not attempt here any explanation of these effects. The explanation naturally rests on a knowledge of the mechanism of rectification in crystals, which is as yet not definitely known. We have simply placed on record the observed effects of heat, ultra-violet light, and X-rays on the rectifying action of crystals *.

Our thanks are due to Mr. Bhagabati Chanar Guha for his kind assistance in running the X-ray tube.

Physics Laboratory,
Dacca University.
Oct. 10th, 1934.

* A theory of contact-point rectification has been proposed elsewhere by one of the authors (S. R. Khastgir). According to the theory, the rectification in the *ionic* crystals, which do not exhibit *volume rectification*, is due to the unbalanced electrostatic force on the crystal surface. In the investigations by the authors, the *carborundum*, *zincite*, and *silicon* crystals showed *volume rectification*, while the rest of the crystals under examination (viz., iron pyrites, galena, magnetite, molybdenite, etc.) showed no such rectification when tested with low-frequency alternating current. Many observed facts about contact-point rectification, including the effects described in this paper, can be explained according to the theory. The details of the theory in relation to the experimental results are given in a paper which is in the course of publication in the 'Indian Journal of Physics.'

XLIX. *The Thermodynamics of Magnetization.*

By Edmund C. Stoner, *Ph.D.* (*Cambridge*), *Reader in Physics at the University of Leeds* *.

1. *Introductory.*

IT is well known that by the application of general thermodynamic arguments a number of conclusions can be drawn about the variation of magnetization with field and temperature, the change of temperature with change of field under adiabatic conditions, and similar questions. The various thermodynamic relations are of considerable value in clearing the ground for a molecular treatment of the effects, which is particularly useful when the molecular theory is as complicated as it is for ferromagnetics; in providing a check on experimental results; and in indicating, in some cases, convenient methods for the determination of particular significant coefficients which may be required. In this paper a systematic derivation will be given of the more important of these thermodynamic relations.

The derivations in original papers of the relations which are of magnetic interest are somewhat scattered; they are usually given incidentally, and confusion is liable to occur owing to the use of different conventions as to symbolism without adequate explanation; and it is sometimes difficult to distinguish between the purely thermodynamic results and those depending on some particular hypothesis. In treatises dealing with magnetism, thermodynamic arguments are also usually introduced incidentally, though there are excellent short sections on thermodynamics in the articles by Debye[1] and Bloch[2] in the first and second editions of the 'Handbuch der Radiologie,' and a brief treatment of some particular topics by Weiss and Foëx[3] in 'Le Magnétisme.' In treatises on thermodynamics the applications to magnetism are seldom considered at all. For these reasons it seems desirable to give a systematic presentation of the thermodynamics of magnetization which serves to bring out a number of significant interconnexions, even though many of the results themselves are not essentially new. The aim will be to make clear the

* Communicated by Prof. R. Whiddington, F.R.S.

information which can be obtained by purely thermodynamic arguments, without introducing a molecular standpoint. Applications will not be made here to particular substances, and the relevant experimental results will be only briefly referred to, as detailed accounts are readily accessible.

In the discussion of the thermodynamics of magnetization it will be sufficient to consider systems of one component and one phase. The relations which hold for such a system when the only forces are those arising from a uniform pressure are well known. Two quantities are required to determine the state of the system, say the temperature and pressure. When a magnetic field is present, another quantity must be known in order that the state may be determined, either the magnetic field or the magnetic moment. Formally, then, the thermodynamic consideration of magnetization requires an extension of the treatment from that appropriate for two " degrees of freedom " (in the phase-rule sense) to that appropriate for three.

There are a number of methods by which particular thermodynamic relations may be derived, but the most convenient general method is based on the introduction of a series of thermodynamic functions of state appropriate to the choice of independent variables. Such are the energy, E, appropriate to the choice of entropy, S, and volume, V, as variables, the total heat, H, for entropy and pressure as variables. The character of this method will first be indicated as applied to a system in the absence of a field of force (2), in order that the relation between the appropriate functions with and without a magnetic field may be clearly brought out. (For details of the method Guggenheim's ' Modern Thermodynamics ' [4] may be referred to, where it is presented with great clearness ; his symbolism will be followed as far as possible.)

The method will then be extended in the manner appropriate for a system in a magnetic field, and a number of general relations will be obtained (3). In dealing with magneto-thermal relations (4) it is usually permissible to " neglect " the volume (or pressure) changes associated with changes in magnetization ; in these circumstances the system may be regarded as having two degrees of freedom, and the thermodynamic relations take a very

simple form. They may, in fact, be obtained from the usual well-known relations merely by substituting H (magnetic field) and $-M$ (M, magnetization) for P and V. This simplification will be briefly considered.

A certain amount of confusion is introduced in the treatment of the thermodynamics of magnetization by the use of the same term "energy" to apply to essentially distinct functions. A brief discussion of magnetic energy is given with reference to the expressions used for the changes in "internal" and "total" energy (5). The relation between the thermodynamic and the statistical treatment is indicated (6).

The general thermodynamic relations are then applied in the discussion of the variation of magnetization with field and temperature (7), and justification is given for the neglect of magnetostriction effects in this discussion (8). General expressions are derived for the specific heats at constant field and constant magnetization (9) and for the magneto-caloric temperature change as a function of field and of magnetization (10). Finally, the magnetostriction relations are briefly considered (11).

One of the most interesting applications of thermodynamic arguments is to questions connected with the internal energy of ferromagnetics; the relevant relations are, therefore, given in such a form as to facilitate this particular application.

2. *System in the Absence of a Field of Force.*

Let E, T, S, P, V be the energy, temperature, entropy, pressure, and volume. For the present the mass of the system may be left undefined. The fundamental equation (for reversible changes—and only these will be considered) is

$$dE = T\,dS - P\,dV.$$

From this equation three others may be derived corresponding to the choice of (S, P), (T, V), and (T, P) as independent variables, with appropriate functions of state in place of E. The four functions and the corresponding equations are given below

E	$dE = T\,dS - P\,dV$,	(2.1)
$H = E + PV$	$dH = T\,dS + V\,dP$,	(2.2)
$F = E - TS$	$dF = -S\,dT - P\,dV$,	(2.3)
$G = E - TS + PV$	$dG = -S\,dT + V\,dP$.	(2.4)

The functions which are defined by these equations are variously referred to. H is referred to as the total heat, or enthalpy; F as the (Helmholtz) free energy, or the force function at constant temperature, or the thermodynamic potential at constant volume; G as the Gibbs free energy, or the thermodynamic potential (at constant pressure).

It should be noted that E represents what may be called either the internal energy or the total energy.

The fact that dE, dH, dF, and dG are exact differentials leads at once to the four Maxwell relations. From (2.3), for example,

$$(\partial S/\partial V)_T=(\partial P/\partial T)_V. \quad . \quad . \quad . \quad . \quad (2.5)$$

Most of the more widely applied thermodynamic relations can be very easily derived from these equations, which form, in fact, a virtually complete summary of the thermodynamics of a simple system. It is unnecessary to consider here the properties of the thermodynamic functions as determinative of equilibrium. It may, however, be noted that if one of the functions is known, for example F, as F(T, V), the others may be expressed in terms of it. Thus

$$E=F+TS=F-T\left(\frac{\partial F}{\partial T}\right)_V=-T^2\left\{\frac{\partial (F/T)}{\partial T}\right\}_V \quad . \quad . \quad (2.6)$$

The importance of this lies in the fact that a statistical treatment may lead to a theoretical expression for F (or to a function closely related to it, such as $\Psi=-F/T$); the energy, entropy, etc., may then be immediately deduced.

3. *System in a Magnetic Field. General Equations.*

Let H be the magnetic field, M the magnetic moment of the system. The fundamental equation may then be written

$$dE=TdS-PdV+HdM. \quad . \quad . \quad . \quad (3.1)$$

This applies to reversible changes. Magnetic energy will be discussed below, and a derivation of the term HdM will be given. A perhaps more familiar form of the equation, applicable to changes whether reversible or irreversible, is

$$dQ=dE+PdV-HdM \quad . \quad . \quad . \quad . \quad (3.2)$$

where dQ is the heat transferred to the system. Corresponding to the choice of M and H as additional independent variables, two equations may be obtained from each of the equations (2.1)–(2.4). These equations, and the corresponding functions, are given below :—

E_1	$dE_1 = T\,dS - P\,dV + H\,dM,$	(3.3)
$E_2 = E_1 - HM$	$dE_2 = T\,dS - P\,dV - M\,dH,$	(3.4)
$W_1 = E_1 + PV$	$dW_1 = T\,dS + V\,dP + H\,dM,$	(3.5)
$W_2 = E_2 + PV$	$dW_2 = T\,dS + V\,dP - M\,dH,$	(3.6)
$F_1 = E_1 - TS$	$dF_1 = -S\,dT - P\,dV + H\,dM,$	(3.7)
$F_2 = E_2 - TS$	$dF_2 = -S\,dT - P\,dV - M\,dH,$	(3.8)
$G_1 = E_1 - TS + PV$	$dG_1 = -S\,dT + V\,dP + H\,dM,$	(3.9)
$G_2 = E_2 - TS + PV$	$dG_2 = -S\,dT + V\,dP - M\,dH.$	(3.10)

Considerable confusion is liable to be caused by the failure to distinguish clearly between such functions as E_1 and E_2 or F_1 and F_2, particularly in passing over to equations appropriate when pressure and volume changes are not explicitly considered. Of the energy functions, E_1 may be referred to as the internal energy, E_2 as the total energy, that is, the sum of the internal energy and the potential energy in the field of force. It is usually F_2 which is referred to as the free energy in dealing with the statistical theory, and it is the total energy, E_2, which is related to it by (2.6). In equations (3.5) and (3.6) the symbol W has been used in place of H in (2.2) to avoid confusion with the symbol H for magnetic field.

4. *Magneto-thermal Relations.*

In considering magneto-thermal relations at constant volume the equations (3.3), (3.4), (3.7), and (3.8) may be used ; at constant pressure equations (3.5), (3.6), (3.9), and (3.10). Both sets of equations give the following series of relations :—

$$(\partial T/\partial M)_S = (\partial H/\partial S)_M, \quad . \quad . \quad . \quad . \quad (4.1)$$

$$(\partial T/\partial H)_S = -(\partial M/\partial S)_H, \quad . \quad . \quad . \quad . \quad (4.2)$$

$$(\partial S/\partial M)_T = -(\partial H/\partial T)_M, \quad . \quad . \quad . \quad . \quad (4.3)$$

$$(\partial S/\partial H)_T = (\partial M/\partial T)_H. \quad . \quad . \quad . \quad . \quad (4.4)$$

The first set of equations shows that these relations hold at constant volume; the second at constant pressure. Thus, from (3.3)

$$(\partial T/\partial M)_{S,V}=(\partial H/\partial S)_{M,V}. \quad . \quad . \quad . \quad (4.5)$$

From (3.5)

$$(\partial T/\partial M)_{S,P}=(\partial H/\partial S)_{M,P}. \quad . \quad . \quad . \quad (4.6)$$

All the relations (4.1)–(4.4) are thus valid either at constant volume or at constant pressure; but this does not imply that $(\partial T/\partial M)_{S,V}$, for example, is necessarily even approximately equal to $(\partial T/\partial M)_{S,P}$; that the difference between them may be negligible in practice is irrelevant to the validity of the relations.

Simplified Treatment.—The above considerations suggest that only four of the equations (3.3)–(3.10) are necessary in deriving the magneto-thermal relations, one being chosen from each of the pairs (3.3, 3.5), (3.4, 3.6), (3.7, 3.9), and (3.8, 3.10); moreover, that the PdV or VdP terms need not be considered. The fundamental equation may then be taken as

$$dE_1=TdS+HdM \quad . \quad . \quad . \quad . \quad (4.7)$$

or

$$dE_2=TdS-MdH, \quad . \quad . \quad . \quad . \quad (4.8)$$

where dE_1 and dE_2 represent the change in internal and in total energy respectively (strictly at constant volume).

The equation (4.7) is then analogous to (2.1), and the magneto-thermal relations may be obtained simply by substituting H and $-M$ (or $-H$ and M) for P and V in the well-known thermodynamic relations. This procedure is justifiable; it does not involve a "neglect" of changes of pressure or volume; for results obtained by the use of the equations to be valid, however, it is essential that in the development of the equations conditions as to constancy of pressure or volume should be consistently applied. This will be specifically discussed below (8) and illustrated in the discussion of the specific heat relations.

5. *Magnetic Energy.*

Internal Energy.—The change in internal energy, at constant entopy and constant volume, is represented in (3.3) and (4.7) by HdM; the relation assumed is

$$(\partial E_1/\partial M)_{S,V}=H. \quad . \quad . \quad . \quad . \quad . \quad (5.1)$$

This relation may be derived from the well-known result according to which magnetic energy may be regarded as distributed at the rate $\mu H^2/8\pi$ per unit volume, where μ is the permeability. Let B be the induction, I the intensity of magnetization, E_1' the internal magnetic energy of a system of volume V :

$$\left.\begin{aligned} I &= M/V, \\ E_1'/V &= \mu H^2/8\pi = B^2/8\pi\mu. \end{aligned}\right\} \quad . \quad . \quad . \quad (5.2)$$

For the change in energy associated with a change dB in the induction

$$d(E_1'/V) = \frac{B\,dB}{4\pi\mu} = \frac{1}{4\pi}(H\,dB). \quad . \quad . \quad . \quad (5.3)$$

Now $B = H + 4\pi I$, so for the change in energy associated with a change dI in the intensity of magnetization

$$\left.\begin{aligned} d(E_1'/V) &= H\,dI, \\ dE_1' &= H\,dM, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (5.4)$$

giving the relation (5.1) above. An alternative derivation is given by Debye[1].

Total Energy.—The change in total energy at constant entropy and volume is represented in (3.4) and (4.8) by $-M\,dH$; the relation assumed is

$$(\partial E_2/\partial H)_{S,\,V} = -M. \quad . \quad . \quad . \quad . \quad (5.5)$$

In dealing with this change it is necessary to consider the work done, at constant magnetization, on external systems to which the field is due, when there is a change in the field ; this change may be associated with a change in the coordinates specifying the external systems. It will be sufficient to consider a simple case, in which the system is an elementary magnet of moment μ_1 in the field due to a second magnet of moment μ_2. Let r be the distance between μ_1 and μ_2. The field due to μ_1 at r is given by

$$\mathbf{H} = \frac{1}{r^3}\{3(\mu_1)_r - \mu_1\}, \quad . \quad . \quad . \quad . \quad (5{\cdot}6)$$

where $(\mu_1)_r$ is the component of μ_1 along r. The work done by μ_1, and hence the decrease in energy $-d\epsilon$, in a displacement of μ_2 in which r increases by dr (the

orientation of the magnets remaining unchanged), is given by

$$f_r dr = -d\epsilon = \frac{\partial}{\partial r}\left[\frac{1}{r^3}\{3(\mu_1)_r.\mu_2 - \mu_1.\mu_2\}\right]dr$$

$$= \mu_1 \frac{\partial}{\partial r}\left[\frac{1}{r^3}\{3(\mu_2)_r - \mu_2\}\right]dr$$

$$= \mu_1 . d\mathbf{H}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.7)$$

where dH is the change of the field due to μ_2 at μ_1. The result here obtained is for a case in which the external system is specified by a single coordinate. If the system is specified by coordinates $q_1, q_2 \ldots$,

$$\Sigma\, d\epsilon = -\mu_1 \Sigma(\partial \mathbf{H}_k/\partial q_k)dq_k = -\mu_1 . d\mathbf{H}. \quad . \quad (5.8)$$

A system of moment **M** may be regarded as built up of a number of elementary magnets $\mu_1, \mu_2 \ldots$, so that

$$d\mathrm{E}_2' = -\mathbf{M}.d\mathbf{H}, \quad . \quad . \quad . \quad . \quad . \quad (5.9)$$

giving the relation above. A somewhat similar derivation of this relation is given by Bloch [2].

Energy in the Absence of an External Field.—The internal energy, E_1, as well as the total energy, E_2, must be distinguished from the energy of the system in the absence of a field, which will be denoted by E_0. The difference between E_1 and E_2 is given by the first of the equations (3.4), namely,

$$\mathrm{E}_1 - \mathrm{E}_2 = \mathrm{MH}. \quad . \quad . \quad . \quad . \quad (5.10)$$

A general equation of this type cannot be given for $\mathrm{E}_1 - \mathrm{E}_0$; experimental results for particular substances (or classes of substances) must be considered. If the value of M as f(H, T) is known, for example, the value of $(\partial \mathrm{E}_1/\partial \mathrm{M})_\mathrm{T}$ may be derived from the thermodynamic relations; alternatively, a particular assumption as to the value of $(\partial \mathrm{E}_1/\partial \mathrm{M})_\mathrm{T}$ may be made, and the form of f(H, T) consistent with it may be deduced. These two methods will be followed below, and their relative values will be discussed.

6. *Relation between the Thermodynamic and Statistical Treatment.*

In a statistical treatment [5] the development proceeds from an assumption as to the energy of individual molecules

in a magnetic field; from this the energy, and other properties of an aggregate of molecules, are deduced. Once any of the thermodynamic functions has been obtained, the others may be derived from it by the relations (3.3)–(3.10).

If, for example, a molecule has a "permanent" moment μ, and acquires in a field an induced moment αH, the energy in a field is given by

$$\epsilon=\epsilon_0-\boldsymbol{\mu}.\mathbf{H}-\tfrac{1}{2}\alpha H^2. \quad . \quad . \quad . \quad . \quad (6.1)$$

By applying a statistical treatment it may be shown (it is unnecessary to give the details of the calculations here) that, considering the classical case, corresponding to a continuous distribution of orientations of μ relative to H, and further, supposing that $\mu H/kT$ is small, for an aggregate of n molecules

$$E_2=n\epsilon_0-\frac{n\mu^2H^2}{3kT}-\tfrac{1}{2}n\alpha H^2 \quad . \quad . \quad . \quad (6.2)$$

$$M=\frac{n\mu^2H}{3kT}+n\alpha H. \quad . \quad . \quad . \quad . \quad . \quad (6.3)$$

Putting $n\epsilon_0=E_0$, the result for the internal energy E_1 is

$$E_1=E_2+MH=E_0+\tfrac{1}{2}n\alpha H^2. \quad . \quad . \quad . \quad (6.4)$$

E_2, E_1, and E_0 all refer to the system at the same temperature; (6.4) therefore indicates that the internal energy, at constant temperature, of a magnetized body is independent of the field in so far as the magnetization arises from permanent molecular magnets, but that it is field dependent when the magnetization arises from "induced" molecular magnets. The form (6.1) for the energy corresponds, as is obvious from (6.3), to a substance having a paramagnetic susceptibility obeying Curie's law (the molecular susceptibility being $\chi=\mu^2/3kT$), and a diamagnetic susceptibility ($-\alpha$ per molecule) independent of the temperature.

The above simple illustration will serve to indicate the relation between the thermodynamic and the statistical treatment, and to suggest the significance, from a molecular standpoint, of the discussion given below.

7. *Magnetization as a Function of Field and Temperature.*

In dealing with applications of the fundamental thermodynamic relations, it is convenient to consider

a definite quantity of the substance. Unit mass (1 gram), unit volume (1 cm.^{3}), or 1 gram molecule are usually chosen. Here the quantity will be taken as unit mass. The magnetic moment M is then the specific intensity of magnetization, which will be denoted by σ. The same symbols, E, V, and S, will be used, but they will now denote the energy, volume, and entropy per unit mass; V, the specific volume, is equal to $1/\rho$, where ρ is the density. The (volume) intensity of magnetization is given by $I=\rho\sigma$. The heat absorbed per degree rise of temperature will be the usual specific heat, which will be denoted by C. Thus $C_V=T(\partial S/\partial T)_V$.

The magnetization may be represented generally as a function of field and temperature:

$$\sigma=f(H, T). \quad . \quad . \quad . \quad . \quad . \quad (7.1)$$

Different assumptions as to the dependence of the internal energy E_1 on σ or H at constant temperature lead to different forms for the function f. Various assumptions will be made in turn which will be found to give forms for the function corresponding to those found experimentally for different magnetic classes of substances.

Derivation of f (H, T) *from assumed* $(\partial E_1/\partial\sigma)_T$.—

$$(i.) \quad (\partial E_1/\partial\sigma)_T=H. \quad . \quad . \quad . \quad . \quad (7.2)$$

From (4.4)

$$(\partial\sigma/\partial T)_H=(\partial S/\partial H)_T.$$

From (4.7)

$$(\partial S/\partial H)_T=\frac{1}{T}(\partial E_1/\partial H)_T-\frac{H}{T}(\partial\sigma/\partial H)_T$$

$$=\frac{1}{T}(\partial E_1/\partial\sigma)_T(\partial\sigma/\partial H)_T-\frac{H}{T}(\partial\sigma/\partial H)_T$$

$$=0.$$

The assumption (7.2) thus gives

$$\left.\begin{aligned}(\partial\sigma/\partial T)_H&=0,\\ \sigma&=f(H).\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (7.3)$$

For a substance for which σ is proportional to H the susceptibility χ is independent of the temperature. This corresponds to the observed characteristics of normal

diamagnetics, and also of many metallic paramagnetics at ordinary temperatures ; for such substances, therefore the relation (7.2) holds.

$$\text{(ii.)} \quad (\partial E_1/\partial\sigma)_T = 0 \quad . \quad . \quad . \quad . \quad . \quad (7.4)$$

From (4.4) and (4.7)

$$(\partial\sigma/\partial T)_H = \frac{1}{T}(\partial E_1/\partial\sigma)_T(\partial\sigma/\partial H)_T - \frac{H}{T}(\partial\sigma/\partial H)_T$$

$$= -\frac{H}{T}(\partial\sigma/\partial H)_T. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.5)$$

The equation (7.5) is solved by

$$\sigma = f(H/T). \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.6)$$

The form of the function f cannot, of course, be determined by thermodynamic arguments. If, however, it is known that at constant temperature σ is proportional to H—that is, that the susceptibility χ is independent of H—it follows that

$$\chi = \sigma/H = C/T. \quad . \quad . \quad . \quad . \quad . \quad (7.7)$$

where C is constant—that is, Curie's law is obtained. The Langevin formula and its quantum modifications are compatible with the general formula (7.6). The assumption (7.4) can be expected to hold closely only when the distance between the carriers of the magnetic moment is such that any magnetic, as well as any associated, interaction between them can be neglected—that is, for a paramagnetic gas. Curie's law does, in fact, hold closely for oxygen. Even for a paramagnetic gas, however, the relation (7.7) does not necessarily hold, as in the case of nitric oxide, indicating that here the initial assumption (7.4) is invalid. An interpretation of this can be given only from a molecular standpoint.

$$\text{(iii.)} \quad (\partial E_1/\partial\sigma) = -N\rho\sigma. \quad . \quad . \quad . \quad . \quad (7.8)$$

In general the internal energy may be supposed to depend on the magnetization in a manner which can be represented by

$$(E_1)_T = A_T + B_T\sigma^2 + C_T\sigma^4, \quad . \quad . \quad . \quad (7.9)$$

where the coefficients are functions of the temperature.

The assumption (7.8) is equivalent to

$$B_T = -\tfrac{1}{2}N\rho, \quad C_T = 0. \quad . \quad . \quad . \quad (7.10)$$

Whether this assumption (with N independent of T) is applicable to any particular material is a matter to be determined from experiment. The symbol N is adopted in accordance with the customary usage in the Weiss treatment of para- and ferromagnetism; it may be referred to as the molecular field coefficient.

Proceeding as in connexion with (7.4),

$$(\partial\sigma/\partial T)_H = -\{(H+N\rho\sigma)/T\}(\partial\sigma/\partial H)_T. \quad . \quad (7.11)$$

This equation is satisfied by

$$\sigma = f_1\{(H+N'\rho\sigma)/T\} \quad . \quad . \quad . \quad . \quad (7.12)$$

with

$$N' - T(\partial N'/\partial T) = N, \quad . \quad . \quad . \quad . \quad (7.13)$$

as is seen immediately by substitution. The equation (7.13) is compatible with $N' = N + aT$ where a is constant. The result, however, can then be expressed by

$$\sigma = f\{(H+N\rho\sigma)/T\}, \quad . \quad . \quad . \quad . \quad (7.14)$$

with a new function f.

For a substance for which (7.8) holds, and for which the susceptibility is independent of the field,

$$\chi = \sigma/H = C/(T - N\rho C), \quad . \quad . \quad . \quad (7.15)$$

where C is constant. This is the Curie-Weiss law,

$$\chi = C/(T-\theta) \quad \text{with} \quad \theta = N\rho C. \quad . \quad (7.16)$$

The experimental results on many paramagnetics are compatible with (7.14), or, apart from saturation effects, with (7.15), over considerable ranges of temperature. In general, however, there are deviations from a Weiss law, indicating that the assumption (7.8), with N constant, is not strictly applicable. The experimental results for ferromagnetics below the Curie temperature are also in rough agreement with (7.14) if σ is the intrinsic magnetization; but analysis of the results shows that (7.8) is not strictly applicable. Over any considerable temperature range, which extends both below and above the Curie point, N cannot be considered even approximately constant.

$$\text{(iv.)} \quad (\partial E_1/\partial\sigma)_T = -N_T\rho\sigma. \quad . \quad . \quad . \quad . \quad (7.16)$$

If it is supposed that the molecular field coefficient varies with the temperature, as indicated by the suffix in (7.17), results formally similar to (7.12) and (7.13) are obtained :

$$\sigma = f\{(H+N_T'\rho)/T\} \quad . \quad . \quad . \quad . \quad (7.18)$$

with $$N_T' - T(\partial N_T'/\partial T) = N_T. \quad . \quad . \quad . \quad . \quad (7.19)$$

Little purpose is served in developing this result further with the nature of the dependence of N_T (or N_T') on T undefined. It may be noted, however, as pointed out by Weiss[6], that when N is not constant the "energetic" molecular field $N_T\rho\sigma$ differs from the molecular field $N_T'\rho\sigma$ required to "correct" the equation of state.

Derivation of $(\partial E_1/\partial\sigma)_T$ *from observed* f (H, T).—The above discussion shows that it is possible to draw conclusions as to the form of f in (7.1) compatible with different conditions as to the dependence of the internal energy on the magnetization. The derivation of the Curie law (7.7) in this way is the classical example, having been given by Langevin[7]. The relations obtained, however, are much less specifically informative than appears at first sight ; for whether (7.2), (7.8), or (7.16) is the appropriate assumption for a particular substance can be decided only on the basis of a particular hypothesis as to the molecular processes occurring, or of the experimentally determined form of the function which is being deduced. The premises of the treatment given are the assumed value of $(\partial E_1/\partial\sigma)_T$ and the experimental value for $(\partial\sigma/\partial H)_T$; from these, conclusions can be drawn as to $(\partial\sigma/\partial T)_H$. It is much less misleading as to the information obtainable from thermodynamic arguments if use is made of the experimental results for σ as f(H, T) to derive values of $(\partial E_1/\partial\sigma)_T$; this can be done without introducing a molecular standpoint, and the conclusions drawn are of considerable value in the development of a more detailed molecular theory.

From (4.7)

$$(\partial E_1/\partial\sigma)_T = T(\partial S/\partial\sigma)_T + H. \quad . \quad . \quad . \quad (7.20)$$

Using (4.3)

$$(\partial E_1/\partial\sigma)_T = H - T(\partial H/\partial T)_\sigma = -T^2\left\{\frac{\partial}{\partial T}\left(\frac{H}{T}\right)\right\}_\sigma. \quad (7.21)$$

This general relation may be put in the convenient form

$$\left(\frac{\partial E_1}{\partial \sigma}\right)_T = H + \frac{T(\partial\sigma/\partial T)_H}{(\partial\sigma/\partial H)_T} \quad . \quad . \quad . \quad . \quad (7.22)$$

Essentially a purely thermodynamic treatment yields no further information than that contained in (7.22), which at once gives the following results :—

$$\left.\begin{array}{lll} \text{(i.)} & \chi = \text{constant} & (\partial E_1/\partial\sigma)_T = H, \\ \text{(ii.)} & \chi = C/T & (\partial E_1/\partial\sigma)_T = 0, \\ \text{(iii.)} & \chi = C/(T-\theta) & (\partial E_1/\partial\sigma)_T = -\theta\sigma/C = -N\rho\sigma. \end{array}\right\}$$
$$. \quad . \quad . \quad . \quad . \quad (7.23)$$

When the dependence of σ on H and T is more complicated than that represented in (7.23), the simplest procedure is to apply (7.22) directly to the experimental results, as the relations can seldom be accurately represented by convenient functions.

8. *Neglect of Volume Changes.*

The relations (7.20)–(7.23) apply strictly at constant volume, E_1 being considered as a function of T, σ, and V. Measurements of magnetization, however, are made under constant-pressure conditions, and it is desirable to consider how far the neglect of the change in internal energy due to the change in volume accompanying magnetization is justified. An estimate of the order of magnitude of the difference between $(\partial E_1/\partial\sigma)_T$ at constant pressure and at constant volume is required.

Let

$$(\partial E_1/\partial\sigma)_{T,P} - (\partial E_1/\partial\sigma)_{T,V} = \partial\eta/\partial\sigma, \quad . \quad . \quad . \quad (8.1)$$

so that

$$(\Delta E_1)_{T,P} - (\Delta E_1)_{T,V} = \Delta\eta \quad . \quad . \quad . \quad (8.2)$$

for the same change in σ. Then

$$\begin{aligned} \partial\eta/\partial\sigma &= (\partial E_1/\partial V)_{T,\sigma}(\partial V/\partial\sigma)_{T,P} \\ &= k\rho(V - V_0)(\partial V/\partial\sigma)_{T,P}, \quad . \quad . \quad . \quad (8.3) \end{aligned}$$

where k is the bulk modulus.

For dia- and paramagnetics (for which $\sigma = 0$ for $H = 0$) the expression for the magnetostrictive volume change may be written

$$\Delta V = V - V_0 = \tfrac{1}{2} m V_0 H^2 \quad . \quad . \quad . \quad . \quad (8.4)$$

Further,

$$(\partial V/\partial\sigma)_{T,\,P}=(\partial V/\partial H)_{T,\,P}(\partial H/\partial\sigma)_{T,\,P}=(\partial V/\partial H)_{T,\,P}/\chi,$$

giving

$$\partial\eta/\partial\sigma=\tfrac{1}{2}km^2H^3/\chi\rho. \quad . \quad . \quad . \quad . \quad . \quad (8.5)$$

Data are available, from Kaptiza's measurements[8], for the linear magnetostriction of a limited number of dia- and paramagnetics. Much the largest effect was found for bismuth, where it was very small for polycrystalline material; for single crystals a positive magnetostriction was found when the field was along the trigonal axis, and a negative magnetostriction when at right-angles to the axis. The corresponding magnetostriction coefficients m_{33} and m_{11} in the formula

$$\Delta l/l=\tfrac{1}{2}mH^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (8.6)$$

had the values $6{\cdot}6\times10^{-16}$ and -8×10^{-16} at room-temperature. It is probable that the value of $\Delta V/V$ is much less than that of $\Delta l/l$ (as is found for ferromagnetics) in any direction; a value of 8×10^{-16} for m in (8.4) can certainly be taken as an upper limit. For most substances the linear magnetostriction is probably less than a tenth of that for bismuth. Taking $k/\rho=10^{11}$ as a reasonable average value

$$\left.\begin{aligned}\partial\eta/\partial\sigma&<3\times10^{-20}H^3/\chi,\\ \Delta\eta&<3\times10^{-20}H^4.\end{aligned}\right\}. \quad . \quad . \quad . \quad (8.7)$$

This change in energy is clearly negligible for all ordinarily practicable magnetic fields. For diamagnetics for which (7.23 (i.)) holds

$$\Delta\eta/\Delta E_1<3\times10^{-20}H^3. \quad . \quad . \quad . \quad . \quad . \quad (8.8)$$

For paramagnetics for which (7·23 (iii.)) holds, writing $\sigma=\chi H$

$$\Delta\eta/\Delta E_1<6\times10^{-20}H^2/N\rho\chi^2. \quad . \quad . \quad (8.9)$$

For all diamagnetics, and for most paramagnetics, $\Delta\eta$ is negligible in comparison with ΔE_1. For strict Curie law paramagnetics $\Delta E_1=0$; but even in this case $\Delta\eta$ may be neglected owing to its small absolute value under all normal conditions.

For ferromagnetics (8.3) may be considered in the slightly modified form

$$\frac{\Delta\eta}{\Delta\sigma}=\frac{1}{2}\Big/\frac{k}{\rho}\left(\frac{\Delta V}{V}\right)^2\cdot\Delta\sigma. \quad . \quad . \quad . \quad . \quad (8.10)$$

The highest observed value for $(\Delta V/V)$ is of the order 10^{-6} for increase of the (apparent) magnetization from zero to the saturation value ($\sigma=50$–250). This value of $(\Delta\eta/\Delta\sigma)$ is small, and will in general be negligible compared with the value of $(\Delta E_1/\Delta\sigma)$ as given by (7.22). If the intrinsic magnetization is considered, rather than the apparent magnetization, the value of $(\Delta V/V)$, as estimated by Powell[9], is of the order 10^{-3} for iron and nickel, giving (with $k/\rho=10^{11}$)

$$\Delta\eta=0{\cdot}5\times10^{5} \quad . \quad . \quad . \quad . \quad . \quad (8.11)$$

for the change in intrinsic magnetization from zero to the saturation value. This is still small (about a thousandth of a calorie per gram), and is quite negligible in comparison with the total change in energy to be considered in this case, namely

$$\Delta E_1=-\tfrac{1}{2}N\rho\sigma_0^2. \quad . \quad . \quad . \quad . \quad (8.12)$$

For nickel $\sigma_0\doteqdot57$, $N\rho\doteqdot10^5$, indicating that again the magnetostriction may be neglected.

The above discussion shows that the use of the approximate equation

$$dE_1=T\,dS+H\,d\sigma \quad . \quad . \quad . \quad . \quad (8.13)$$

is completely justifiable for all the applications which are ordinarily made. The equation must, of course, be modified when the effect of applied stresses is under consideration.

9. *Specific Heat.*

There are four specific heats to be distinguished, namely, those at constant pressure and constant volume, each at constant magnetization and constant field. The expressions given below are derived from the general equations (3.3)–(3.6), making use of thermodynamic relations derived from the equations (3.3)–(3.10), some of which have already been given explicitly. The derivations are straightforward, and it is unnecessary to give details.

$$C_{V,\sigma}=\left(\frac{\partial E_1}{\partial T}\right)_{V,\sigma}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.1)$$

$$C_{P,\sigma}=\left(\frac{\partial W_1}{\partial T}\right)_{P,\sigma}=\left\{C_V+T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P\right\}_\sigma, \quad (9.2)$$

$$C_{V,H}=\left(\frac{\partial E_2}{\partial T}\right)_{V,H}=\left\{C_\sigma-T\left(\frac{\partial H}{\partial T}\right)_\sigma\left(\frac{\partial\sigma}{\partial T}\right)_H\right\}_V, \quad (9.3)$$

$$C_{P,H}=\left(\frac{\partial W_2}{\partial T}\right)_{P,H}=\left\{C_V+T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P\right\}_H \quad (9.4)$$

$$=\left\{C_\sigma-T\left(\frac{\partial H}{\partial T}\right)_\sigma\left(\frac{\partial\sigma}{\partial T}\right)_H\right\}_P, \quad (9.5)$$

By a treatment similar to that given in the last section it may be shown that

$$(C_H-C_\sigma)_P-(C_H-C_\sigma)_V=0. \quad . \quad . \quad . \quad (9.6)$$

The essential specific heat relation, as far as magnetization is concerned, is thus

$$C_H-C_\sigma=-T\left(\frac{\partial H}{\partial T}\right)_\sigma\left(\frac{\partial\sigma}{\partial T}\right)_H \quad . \quad . \quad . \quad . \quad (9.7)$$

$$\left\{\left(\frac{\partial E_1}{\partial\sigma}\right)_T-H\right\}\left(\frac{\partial\sigma}{\partial T}\right)_H \quad . \quad (9.8)$$

For temperature independent dia- and paramagnetics

$$C_H=C_\sigma. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.9)$$

For paramagnetics (7.23 (ii.) and (iii.))

$$C_H-C_\sigma=\frac{CH^2}{(T-\theta)^2}=\frac{\chi H}{(T-\theta)}. \quad . \quad . \quad (9.10)$$

(C without a suffix is the constant in the Curie-Weiss law.)

This relation will, of course, hold only so long as the susceptibility is independent of the field; it will not be applicable for $T\sim\theta$. In general, for paramagnetics, if θ is positive, the Weiss law breaks down when T approaches θ. Putting $C=\cdot05$, a rough average value,

$$C_H-C_\sigma=\frac{\cdot05}{4\cdot2\times10^7}\frac{H^2}{(T-\theta)^2} \text{ calories per degree per gram.}$$

$$. \quad . \quad . \quad . \quad (9.11)$$

The difference is clearly negligible for all ordinary conditions as to field and temperature.

The most important application of the equations is to ferromagnetics [9], [10]. For $H=0$ a ferromagnetic will

have an "excess specific heat" due to its ferromagnetic properties given by

$$\Delta C = \left(\frac{\partial E_1}{\partial \sigma}\right)_T \left(\frac{\partial \sigma}{\partial T}\right)_{H=0}, \quad . \quad . \quad . \quad (9.12)$$

where σ is the intrinsic magnetization. A rough determination of ΔC is possible in the region below and not too far from the Curie point by subtracting from the observed specific heat the extrapolated value from above the Curie point (where $(\partial\sigma/\partial T)_{H=0}=0$). The degree of accuracy possible in the determination of $(\partial E_1/\partial\sigma)_T$ by this method is limited on the one hand by the uncertainties of the extrapolation, and on the other by uncertainties in the value of $(\partial\sigma/\partial T)_{H=0}$ which are obtained by extrapolation from the observed values of the apparent σ in large fields.

Ratio of Specific Heats: Adiabatic and Isothermal Magnetization. Using the magneto-thermal relations (4·1)–(4·4) the following expressions are obtained for the specific heats (either at constant pressure or at constant volume):—

$$C_H = T\left(\frac{\partial S}{\partial T}\right)_H = T\left(\frac{\partial S}{\partial \sigma}\right)_H \left(\frac{\partial \sigma}{\partial T}\right)_H = -T\left(\frac{\partial H}{\partial T}\right)_S \left(\frac{\partial \sigma}{\partial T}\right)_H, \quad (9.13)$$

$$C_\sigma = T\left(\frac{\partial S}{\partial T}\right)_\sigma = T\left(\frac{\partial S}{\partial H}\right)_\sigma \left(\frac{\partial H}{\partial T}\right)_\sigma = T\left(\frac{\partial \sigma}{\partial T}\right)_S \left(\frac{\partial H}{\partial T}\right)_\sigma. \quad (9.14)$$

These expressions give for the ratio of the specific heats

$$\frac{C_H}{C_\sigma} = \left(\frac{\partial H}{\partial \sigma}\right)\left(\frac{\partial \sigma}{\partial H}\right)_T = \left(\frac{\partial \sigma}{\partial H}\right)_T \Big/ \left(\frac{\partial \sigma}{\partial H}\right)_S, \quad . \quad (9.15)$$

showing that the ratio of the isothermal to the adiabatic differential susceptibility is equal to the ratio of the specific heat at constant field to that at constant magnetization. Of various forms for the expression for the difference in the two susceptibilities the following seem most convenient:—

$$\{(\partial\sigma/\partial H)_T - (\partial\sigma/\partial H)_S\}/(\partial\sigma/\partial H)_T$$
$$= -\frac{T}{C_H}\left(\frac{\partial H}{\partial T}\right)_\sigma \left(\frac{\partial \sigma}{\partial T}\right)_H$$
$$= \frac{1}{C_H}\left\{\left(\frac{\partial E_1}{\partial \sigma}\right)_T - H\right\}\left(\frac{\partial \sigma}{\partial T}\right)_H. \quad (9.16)$$

When the susceptibility is temperature independent, the two susceptibilities are equal. In general, for para- and ferromagnetics the isothermal differential susceptibility will be greater. These expressions have application in experiments such as those of Kapitza[11], in which magnetization takes place under adiabatic conditions.

10. *Magneto-caloric Effect.*

The magneto-caloric effect—the reversible temperature change accompanying adiabatic change of magnetization is of interest not only for ferromagnetics, but also for paramagnetics, in view of its application in the realization of temperatures below 0·1° K. It has been discussed in particular by Weiss and his collaborators[6],[12] in connexion with ferromagnetics, and by Debye[13] and Giauque[14] in connexion with paramagnetics. The following treatment does not differ in essentials, though it possibly brings out certain connexions more clearly. Volume changes may again be neglected.

(i.) $(\partial T/\partial H)_S$.

From (4.2)

$$(\partial T/\partial H)_S = -(\partial\sigma/\partial S)_H = -(\partial\sigma/\partial T)_H(\partial T/\partial S)_H$$
$$= -(T/C_H)(\partial\sigma/\partial T)_H. \quad . \quad . \quad . \quad . \quad . \quad (10.1)$$

For a change of field from 0 to H

$$\log \frac{T'}{T} \doteqdot \frac{\Delta T}{T} = -\int_0^H \frac{1}{C_H}\left(\frac{\partial\sigma}{\partial T}\right)_H dH. \quad . \quad (10.2)$$

Since ΔT is always small, at most about one or two degrees, the approximation for $\log (T'/T)$ will be permissible for ferromagnetics (where the effect is appreciable only at temperatures not very far from the Curie point), but not for paramagnetics near absolute zero.

For a substance for which $\chi = C/(T-\theta)$

$$\Delta T = \frac{1}{2C_H}\frac{T}{T-\theta}\chi H^2. \quad . \quad . \quad . \quad . \quad (10.3)$$

This expression is useful as giving an indication of the order of magnitude of the effect, but in most cases of practical interest the general expression must be used. It is not intended to discuss here the application of the

thermodynamic equations to particular substances, but it may be noted that in the application to ferromagnetics considerable errors may be introduced by treating C_H and $(\partial\sigma/\partial T)_H$ as constants with the values for $H=0$. The value of $(\partial\sigma/\partial T)_H$ decreases numerically with H below the Curie point proper (regarded as the temperature at which the intrinsic magnetization becomes zero with $H=0$) and increases above, while C_H will also vary with H. These questions can be usefully discussed further only with reference to the detailed experimental data.

(ii.) $(\partial T/\partial\sigma)_S$.

The consideration of the temperature change as a function of magnetization is particularly illuminating in connexion with ferromagnetics, as has been shown by Weiss with reference to the molecular field hypothesis. The general relations are readily obtained.

From (4.1)

$$\begin{aligned}(\partial T/\partial\sigma)_S &= (\partial H/\partial S)_\sigma = (\partial H/\partial T)_\sigma(\partial T/\partial S)_\sigma \\ &= (T/C_\sigma)(\partial H/\partial T)_\sigma \\ &= (1/C_\sigma)\{H-(\partial E_1/\partial\sigma)_T\}. \quad . \quad . \quad . \quad . \quad (10.4)\end{aligned}$$

Similar remarks apply in connexion with the expressions for $(\partial T/\partial\sigma)_S$, as applied to ferromagnetics, as with those for $(\partial T/\partial H)_S$. If $(\partial E_1/\partial\sigma)_T=-N\rho\sigma$,

$$\Delta T = \frac{1}{C_\sigma}\int_{\sigma_0}^{\sigma}(H+N\rho\sigma)\,d\sigma. \quad . \quad . \quad . \quad (10.5)$$

In this form the expression has been applied by Weiss.

Below the Curie point $N\rho\sigma >> H$, and

$$\Delta T=(N\rho/2C_\sigma)(\sigma^2-\sigma_0^2), \quad . \quad . \quad . \quad . \quad (10.6)$$

where σ_0 is the intrinsic magnetization in zero applied field. Above the Curie point,

$$\Delta T=(1/2C_\sigma)(1/\chi+N\rho)\sigma^2. \quad . \quad . \quad . \quad (10.7)$$

In general, near the Curie point $N\rho >> 1/\chi$, and

$$\Delta T=(1/2C_\sigma)N\rho\sigma^2. \quad . \quad . \quad . \quad . \quad . \quad (10.8)$$

If the susceptibility is given by $\chi=C/(T-\theta)$, since $\theta=N\rho C$,

$$\Delta T=\frac{1}{2C_\sigma}\left[\frac{T-\theta}{C}+\frac{\theta}{C}\right]\sigma^2$$

$$= \frac{T}{2C_\sigma}\frac{\sigma^2}{C} = \frac{1}{2C_\sigma}\frac{T}{T-\theta}\frac{\sigma^2}{\chi}. \quad . \quad . \quad (10.9)$$

This expression may be compared with (10.3). In applications it is usually necessary to make use of the general expression (10.4).

The magneto-caloric effect has been carefully investigated for a number of ferromagnetics. It may be noted that it does not provide information additional to that obtainable from the experimental results for C_H and for σ as $f(H, T)$; but it enables estimates of $(\partial E_1/\partial\sigma)_T$ to be made fairly directly, and this is possible otherwise only from an elaborate experimental investigation of the σ, H, T relations and a detailed analysis of the results.

11. *Magnetostriction.*

From the general equations (3.3)–(3.10) a series of relations similar to the magneto-thermal relations may be obtained. The following is typical:

$$(\partial V/\partial H)_P = -(\partial\sigma/\partial P)_H. \quad . \quad . \quad . \quad . \quad (11.1)$$

This, and the other relations, may be obtained by replacing S and T in (4.1)–(4.4) by V and $-P$; they then hold either at constant temperature or at constant entropy. The relations for a uniform pressure, however, are of less practical interest than those for an applied tension. Consider a rod of length l, cross-section A; let F be the applied force. The "simplified" equation referred to unit mass may then be written

$$dE_1' = H\,d\sigma + \frac{1}{\rho A l}F\,dl$$

$$= H\,d\sigma + \frac{1}{\rho l}Z\,dl = H\,d\sigma + \frac{1}{\rho}Z\,d\lambda, \quad . \quad . \quad (11\ 2)$$

where Z is the longitudinal tension and $\lambda = \Delta l/l$.

Let

$$W_2' = E_1' - H\sigma - \frac{1}{\rho}Z\lambda.$$

Then

$$dW_2' = -\sigma\,dH - (\lambda/\rho)dZ,$$

giving $(\partial\sigma/\partial Z)_H = (1/\rho)(\partial\lambda/\partial H)_Z$

or $(\partial I/\partial Z)_H = (\partial\lambda/\partial H)_Z. \quad . \quad . \quad . \quad . \quad . \quad (11.3)$

This is the most useful of the relations. The others may easily be derived. They apply either at constant entropy or constant temperature.

The volume magnetostriction associated with the intrinsic magnetization of ferromagnetics is of particular interest. It makes itself apparent in the anomalous thermal expansion, which is particularly marked in the neighbourhood of the Curie point. At constant temperature and field the volume is determined by

$$(\partial F_2/\partial V)=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (11.4)$$

For the present purpose it is convenient to consider F, E, and V referred not to unit mass, but to a system as a whole, whose mass, say m, will be constant. At zero field, F_2 may be regarded as made up of two parts, F_2', which is independent of the magnetization, M, and which would correspond to normal properties, and F_2'', which is dependent on M, being equal to the M-dependent part of the internal energy E_1, say E_1''. The excess volume due to M is therefore determined by

$$\partial F_2''/\partial V=-\partial E_1''/\partial V. \quad . \quad . \quad . \quad (11.5)$$

The isothermal bulk modulus k is given by

$$k=V\frac{\partial^2 F_2'}{\partial V^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (11.6)$$

Integration of this equation, subject to the usual conditions, gives

$$\partial F_2'/\partial V=k\Delta V/V,$$

so that

$$\frac{\Delta V}{V}=-\frac{1}{k}\frac{\partial E_1''}{\partial V}. \quad . \quad . \quad . \quad . \quad . \quad (11.7)$$

In the equations (11.4)–(11.7) E_1, F_2, and V refer to the constant mass m, and the differentiation with respect to V is carried out subject to the condition that the total magnetization, M, and also the mass are constant. If the magnetic energy per unit mass is $-\frac{1}{2}N\rho\sigma^2$

$$E_1''=-\tfrac{1}{2}mN\rho\sigma^2=-\tfrac{1}{2}N\rho(m\sigma)^2/m=-\tfrac{1}{2}N\rho M^2/m,$$

so that

$$\frac{\partial E_1''}{\partial V}=-\frac{1}{2}\frac{M^2}{m}\frac{\partial(N\rho)}{dV}.$$

Inserting this value in (11.7), and substituting $\rho\sigma V$ for M,

$$\frac{\Delta V}{V} = \frac{\rho\sigma^2 V}{2k} \frac{\partial(N\rho)}{\partial V} \quad . \quad . \quad . \quad . \quad . \quad (11.8)$$

If $N\rho$ increases with increase of V, $\Delta V/V$ is positive, as for iron; if it decreases, $\Delta V/V$ is negative, as for nickel.

A more elaborate statistical treatment of this effect has been given by Powell[9]; the final result is equivalent to that obtained by substituting for E_1'' the magnetization-dependent energy as given by a slight modification of the Heisenberg theory. It then follows that the interchange interaction, J_0, increases with increasing interatomic distance for iron, and decreases for nickel. The above treatment gives essentially a simple way of arriving at a general result, expressed by (11.7), whose significance, in terms of the formal molecular field hypothesis, is clearly shown by (11.8).

Summary.

A systematic derivation is given of the more important thermodynamic relations for magnetization. The equations for the appropriate thermodynamic functions are obtained, and the general magneto-thermal relations derived. Magnetic energy is discussed, and a derivation of the magnetic terms in the general equations is given, the distinction between " internal " and " total " energy being pointed out. A justification is given of the simplified treatment rendered possible by neglect of the pressure, volume term. The general relations are then applied in the consideration of magnetization, σ, as a function of field, H, and temperature, T. It is shown that essentially a thermodynamic treatment enables the rate of change of the internal energy with σ to be deduced from the experimental σ, H, T relations. General expressions are obtained for the specific heat at constant field and magnetization, and for the magneto-caloric temperature change as $f(H)$ and $f(\sigma)$, the particular forms for special magnetic classes of substances being noted. The magneto-striction relations are briefly considered.

References.

(1) P. Debye, ' Handbuch der Radiologie,' vi. p. 742 (1925).
(2) F. Bloch, ' Handbuch der Radiologie,' vi. ii. p. 378 (1934).
(3) P. Weiss and G. Foex, ' Le Magnétisme,' ch. ix. (Paris: Colin, 1925).

(4) E. A. Guggenheim, 'Modern Thermodynamics.' (Methuen, 1933).
(5) R. H. Fowler, 'Statistical Mechanics' (Camb. Univ. Press, 1929).
(6) P. Weiss, *Ann. de Phys.* xvii. p. 97 (1932).
(7) P. Langevin, *Ann. de Chim. et de Phys.* v. p. 70 (1905).
(8) P. Kapitza, Proc. Roy. Soc. A, cxxxv. p. 568 (1932).
(9) F. C. Powell, Proc. Phys. Soc. xlii. p. 390 (1930).
(10) E. Lapp, *Ann. de Phys.* xii. p. 442 (1929).
(11) P. Kapitza, Proc. Roy. Soc. A, cxxxi. p. 244 (1931).
(12) P. Weiss and R. Forrer, *Ann. de Phys.* v. p. 153 (1926).
(13) P. Debye, *Ann. der Phys.* lxxxi. p. 1154 (1926).
(14) W. F. Giauque, J. Amer. Chem. Soc. xlix. p. 1864 (1927).

Physics Department, Leeds University.
December, 1934.

L. *The Specific Thermodynamic Properties of Aqueous Solutions of Strong Electrolytes.* *By* E. A. Guggenheim, *Department of Chemistry, University of Reading**.

1. *Activity Coefficients and Osmotic Coefficients.*

WHEREAS various forms of the so-called "laws of ideal solutions" have been used which are not mutually consistent except at infinite dilution[12], it has been proved by statistical mechanical considerations[13] that for dilute solutions, in which the mutual interaction between the solute particles can be ignored, the chemical potential μ_s of each solute species s is of the form

$$\mu_s=\mu_s^0(\mathrm{T},\mathrm{P})+\mathrm{RT}\log \mathrm{N}_s, \quad . \quad . \quad . \quad . \quad (1)$$

where μ_s^0 is, for a given solvent, a function only of the absolute temperature T and the pressure P, R is the gas constant and N_s the mole fraction of the species s. The chemical potential $\mu_{\mathrm{H_2O}}$ of the solvent, which we shall take to be water, is then given by a formula of exactly the same type,

$$\left.\begin{aligned}\mu_{\mathrm{H_2O}}&=\mu_{\mathrm{H_2O}}^0(\mathrm{T},\mathrm{P})+\mathrm{RT}\log \mathrm{N}_{\mathrm{H_2O}}\\&=\mu_{\mathrm{H_2O}}^0(\mathrm{T},\mathrm{P})+\mathrm{RT}\log\Big(1-\sum_s \mathrm{N}_s\Big)\end{aligned}\right\}, \quad . \quad . \quad . \quad (2)$$

where $\mu_{\mathrm{H_2O}}^0$ is the chemical potential of pure water at the given temperature and pressure. It is, therefore, most reasonable to choose these formulæ as defining ideal solutions. This choice is equivalent to defining an ideal

* Communicated by Prof. F. G. Donnan, C.B.E., M.A., F.R.S.

solution as one in which the solute and solvent species obey respectively Henry's law and Raoult's law in the following form :—

The partial vapour pressure p_i of any species, whether solute or solvent, is, at constant temperature T and *constant external pressure* P, directly proportional to its mole fraction N_i. This formulation of the laws of ideal solutions is due to G. N. Lewis and to Washburn [25], [40].

In the treatment of non-ideal solutions the most convenient functions for measuring deviations from ideality are the activity coefficients and the osmotic coefficient. Unfortunately these coefficients have also been given various definitions which are not entirely equivalent to one another except at very high dilutions. If these coefficients are to be true measures of ideality, and so be equal to unity in any ideal solution, they must be related to the chemical potentials in the following manner. We define the activity coefficient f_s of each solute species by

$$\mu_s = \mu_s^0(\mathrm{T, P}) + \mathrm{RT} \log \mathrm{N}_s f_s, \quad . \quad . \quad . \quad . \quad (3)$$

where μ_s^0 (T, P) is, for a given solvent, independent of the composition of the solution, and f_s tends to unity at infinite dilution of all the solute species. For the solvent, which we take to be water, we similarly define the activity coefficient $f_{\mathrm{H_2O}}$ and the osmotic coefficient g by

$$\left.\begin{aligned} \mu_{\mathrm{H_2O}} &= \mu^0_{\mathrm{H_2O}}(\mathrm{T, P}) + \mathrm{RT} \log \mathrm{N}_{\mathrm{H_2O}} f_{\mathrm{H_2O}} \\ &= \mu^0_{\mathrm{H_2O}}(\mathrm{T, P}) + g\,\mathrm{RT} \log \mathrm{N}_{\mathrm{H_2O}} \\ &= \mu^0_{\mathrm{H_2O}}(\mathrm{T, P}) + g\mathrm{RT} \log (1 - \Sigma \mathrm{N}_s) \end{aligned}\right\} . \quad . \quad (4)$$

It is clear from (4) that the alternatives for using $f_{\mathrm{H_2O}}$ or g are mathematically equivalent, since the two quantities are related by the identity

$$1 - g = \frac{\log f_{\mathrm{H_2O}}}{\log \mathrm{N}_{\mathrm{H_2O}}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

In practice g is the more convenient function, largely for numerical reasons, especially in dealing with very dilute solutions. For example, in a centimolal aqueous solution of a uni-univalent electrolyte the approximate values of the mean activity coefficient f_s of the solute

and of the osmotic coefficient g are respectively 0·90 and 0·97, whereas the activity coefficient f_{H_2O} of the solvent has the more awkward value 1·00001, which is so close to unity as to suggest, erroneously, that the solution is very nearly ideal. For this reason we shall always use the osmotic coefficients to the exclusion of the activity coefficient f_{H_2O} of the solvent. According to the Gibbs-Duhem relation [16],

$$\sum_s N_s d\mu_s + N_{H_2O} d\mu_{H_2O} = 0 \text{ at constant T, P} ; \quad . \quad . \quad (6)$$

the osmotic coefficient g is related to the activity coefficients f_s of the various solute species according to [3]

$$N_{H_2O} d\left\{(1-g)\log \frac{1}{N_{H_2O}}\right\} = -\Sigma N_s \, d\log f_s. \quad . \quad (7)$$

The activity coefficient f_s and osmotic coefficient g, defined as above, may conveniently be referred to as "rational" coefficients, to emphasize the fact that they all have the value unity in any ideal solution, and to contrast them with the "practical" activity coefficients γ_s and practical osmotic coefficient ϕ defined by the formulæ

$$\mu_s = \mu_s^{0'}(T, P) + RT \log m_s\gamma_s, \quad . \quad . \quad . \quad . \quad (8)$$

$$\mu_{H_2O} = \mu^0_{H_2O}(T, P) - \phi \frac{RT}{55{\cdot}5} \sum_s m_s, \quad . \quad . \quad . \quad (9)$$

where m_s denotes the molality (moles/1000 g. solvent) of the solute s and 55·5 is the molality of the pure solvent. Incidentally $1-\phi$ is the same as the function j used by Lewis and Randall [27]. From the Gibbs-Duhem relation (6) it is easy to show [3] that the practical coefficients ϕ and γ_s are related according to

$$d\{\sum_s m_s(1-\phi)\} = -\sum_s m_s d\log\gamma_s. \quad . \quad . \quad (10)$$

These "practical" coefficients are generally used by most authors for expressing their experimental data, but they have no possible advantage over the rational coefficients except that their computation from the experimental data involves slightly less trouble for the former than for the latter. In the present paper we shall consistently use the rational coefficients. The relations

between the rational and the practical coefficients in dilute aqueous solutions are the following :

$$f_s = \gamma_s(1 + 0{\cdot}018 \sum_s m_s), \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

$$g = \phi(1 + 0{\cdot}009 \sum_s m_s). \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Formula (11) is exact, but (12) is an approximation in which terms of the order $(0{\cdot}018 \sum_s m_s)^2$ are neglected. According to (11) we see that in a decimolal solution of a binary electrolyte the difference between the rational activity coefficient f_s and the practical activity coefficient γ_s is 0·36 per cent. ; the corresponding difference between the two kinds of osmotic coefficient is 0·18 per cent. This difference is slightly greater than the probable experimental error of the most accurate experimental data. It therefore seems just worth while recomputing all such data in terms of rational coefficients. In dealing with more concentrated solutions the distinction would, of course, be much more important, as the difference is directly proportional to the total solute molality.

The most accurate experimental method for determining the osmotic coefficient is by means of freezing-point measurements. The freezing-point depression θ of dilute aqueous solution is given in degrees centigrade by [16]

$$\theta(1 + 0{\cdot}00048\theta) = g1{\cdot}858 \times \frac{1000}{18} \log (1 - \sum_s N_s)$$

$$= \phi 1{\cdot}858 \sum_s m_s \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

from which we see that each freezing-point measurement gives a value of g just as directly as of ϕ, only the computation is slightly more laborious. With regard to the correction term $0{\cdot}00048\,\theta$ on the left, the theoretical value of the numerical coefficient is $\frac{1}{T^\circ} - \frac{\Delta c}{2L}$, where T° denotes the absolute temperature of the freezing-point, L is the molal heat of fusion of the solvent, and Δc is the excess of the molal heat capacity of the solid solvent over that of the liquid. When the solvent is water, T° has the value 273·1, L is 1438 calories, and Δc is 9·14 calories/degree. Hence the value of $\frac{1}{T^\circ}$ is 0·00366

and that of $\frac{\Delta c}{2L}$ is 0·00318. It is an accident that these two terms are so nearly equal to each other, and their difference, 0·00048, therefore so small. Actually the correction term $0{\cdot}00048\,\theta$ may be neglected, because at very low concentrations it is less than the experimental error in θ, and at higher concentrations it is outweighed by the uncertainty of about 1 part in 2000 in the value of the coefficient 1·858 on the right. It is, as explained above, just a fortunate accident that this correction term is so small for water. For other solvents it will generally be appreciable.

The most accurate method for the experimental determination of the mean activity coefficient of an electrolyte is the electrometric. For example, the electromotive force E of a cell such as

$$\mathrm{Ag}\,|\,\mathrm{AgCl}\;\left|\begin{matrix}\text{Aqueous solution containing}\\ \mathrm{H^+}\text{ and }\mathrm{Cl^-}\end{matrix}\right|\;\mathrm{H_2},\ \mathrm{Pt}$$

is given by [27], [16]

$$\mathrm{E}=\mathrm{E^0}+\frac{\mathrm{RT}}{\mathrm{F}}\log m_{\mathrm{H}}m_{\mathrm{Cl}}\gamma^2_{\mathrm{H,C}}$$

$$=\left(\mathrm{E^0}+\frac{\mathrm{RT}}{\mathrm{F}}2\log 55{\cdot}5\right)+\frac{\mathrm{RT}}{\mathrm{F}}\log \mathrm{N_H}\mathrm{N_{Cl}}f^2_{\mathrm{H,Cl}},\quad .\quad (14)$$

where $\mathrm{E^0}$ is independent of the composition of the aqueous solution, F is the faraday, $\gamma_{\mathrm{H,Cl}}$ is the practical mean activity coefficient of HCl, and $f_{\mathrm{H,Cl}}$ is the corresponding rational activity coefficient.

Another method of studying activity coefficients experimentally is by means of solubility measurements. Suppose a certain solution to be saturated with respect to the solid phase of an electrolyte whose molecule yields q_+ cations and q_- anions, and let the molality of the cations and anions in the saturated solution be m_+ and m_- respectively. We may then define the mean solubility $s_\pm$ of the electrolyte by

$$(s_\pm)^{q_++q_-}=(m_+)^{q_+}(m_-)^{q_-}.\quad .\quad .\quad .\quad .\quad .\quad (15)$$

The mean solubility in various solutions is then related to the practical activity coefficient $\gamma_\pm$ by the simple formula [27], [16]

$$s_\pm\gamma_\pm=\text{constant}\quad .\quad .\quad .\quad .\quad .\quad (16)$$

and to the rational activity coefficient $f_{\pm}$ by the formula

$$s_{\pm}f_{\pm} = \text{constant}\,(1+0{\cdot}018\sum_s m_s). \quad . \quad . \quad (17)$$

These formulæ have been used for computing rational activity coefficients from the available experimental data.

Although the difference between the values of the rational and the practical coefficients is appreciable, it is in dilute solutions relatively small. Moreover, in dilute solutions these coefficients do not differ greatly from unity, so that the quantities $1-g$ and $\log f_s$ are small compared with unity. It is, therefore, permissible to replace the exact but somewhat awkward relation (7) between the rational coefficients g and the f_s by the simpler approximate relation

$$d\{\sum_s m_s(1-g)\} = -\sum_s m_s d\log f_s, \quad . \quad . \quad . \quad (18)$$

of the same form as the relation (10) between the practical coefficients ϕ and γ_s. Alternatively, and with the same degree of accuracy, we may use the relation

$$d\{\sum_s c_s(1-g)\} = -\sum_s c_s d\log f_s, \quad . \quad . \quad . \quad (19)$$

where c_s denotes the volume concentration of the solute species s. If there is only one solute species, (19) simplifies to

$$d\{c(1-g)\} = -cd\log f. \quad . \quad . \quad . \quad . \quad (20)$$

As a simple and useful example of the application of (20), let us take the case that $\log f$ can be expressed as a sum of powers (not necessarily integral powers) of c,

$$\log f = \sum_r \mathrm{A}_r c^r, \quad . \quad . \quad . \quad . \quad . \quad (21)$$

where the r's are not necessarily integral. Then, by applying (20), we obtain as the formula for $1-g$

$$1-g = \sum_r \frac{r}{r+1}\mathrm{A}_r c^r, \quad . \quad . \quad . \quad . \quad . \quad (22)$$

so that $1-g$ is also expressible as a sum of the same powers of c.

2. *Solutions of Electrolytes.*

When Bjerrum[2], in 1909, first suggested that the typical strong electrolytes are completely dissociated in

dilute aqueous solutions, he at the same time explained that the deviations of such solutions from ideality are due to the electrostatic field of force of the ionic charges. He also pointed out that the magnitude of these deviations is determined primarily by the concentrations and charges of the various ions, and only to a less extent by their individual specific properties.

The first attempt to calculate the effect of the interionic forces on the thermodynamic properties was made by Milner[30] in 1912. The fundamental principles of his treatment are unexceptional, but, owing to the great mathematical difficulties of the problem, he was unable to obtain any exact explicit formulæ. However, the results of his approximate computations may be described by stating that for small concentrations of a symmetrical electrolyte of valence type $(z, -z)$ the osmotic coefficient g behaves approximately according to the law

$$1-g=\alpha z^3 c^{1/2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

where c is the volume concentration of the electrolyte and α is a constant depending on the temperature and dielectric constant of the solvent. The best value of α remained somewhat uncertain. A table of numerical values for α in water at 0° C. given by Milner corresponds fairly closely with formula (23), with the value 0·47 for α, the concentration being expressed in moles of electrolyte per litre. On the other hand, an approximate algebraic formula given by Milner in a footnote corresponds to a value of 0·26 for α.

As the experimental data for all electrolytes cannot be accurately expressed by the formula of the type (23), with a single value for α, Brönsted[6] proposed in 1922 the formula for solutions of single symmetrical electrolytes

$$1-g=\alpha' c^{1/2}+\beta c, \quad . \quad . \quad . \quad . \quad . \quad (24)$$

where α' depends only on the valencies $\pm z$ of the ions, while β varies from one electrolyte to another. According to this formula, at very high dilutions the first term will be the more important one, while specific differences between electrolytes of the same valence type, being taken account of by the second term, will become relatively more important as the concentration increases. It is easy to show by dimensional analysis that the constant α' in (24) must be proportional to the cube of

the numerical valency of the ions. We may, therefore, rewrite (24) in the form

$$1-g=\alpha z^3 c^{1/2}+\beta c, \quad . \quad . \quad . \quad . \quad . \quad (25)$$

where α is the same for all symmetrical electrolytes whatever the valencies $\pm z$. This formula, though empirical, is of great importance as the prototype of formulæ showing specific differences between individual electrolytes, but converging to a uniform limiting law at infinite dilution common to all electrolytes of the same type.

The most important theoretical advance in the treatment of electrolytes is due to Debye and Hückel[9]. By an ingenious and bold artifice[10] they completely avoided the mathematical difficulties of Milner's treatment, and obtained explicit formulæ for the deviations from ideality. The exact formulæ corresponding to their treatment are the following. The rational osmotic coefficient g in aqueous solution at 0° C. is given by

$$1-g=0{\cdot}374\mathrm{I}^{1/2}\frac{\sum_i \mathrm{N}_i z_i^2}{\sum_i \mathrm{N}_i}\frac{\mathrm{N}_{\mathrm{H_2O}}+\sum_i \mathrm{N}_i}{\mathrm{N}_{\mathrm{H_2O}}\mathrm{V}_{\mathrm{H_2O}}+\sum_i \mathrm{N}_i \mathrm{V}^i}$$

$$\times \frac{\sum_i \mathrm{N}_i}{-\log\left(1-\sum_i \mathrm{N}_i\right)} \cdot \sigma\left(\frac{a}{3{\cdot}08}\mathrm{I}^{1/2}\right), \quad . \quad (26)$$

where the suffix i refers to the various ionic species, N denotes a mole fraction and V a partial molal volume. I is the ionic strength defined by

$$\mathrm{I}=\tfrac{1}{2}\sum_i z_i^2 c_i. \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

Finally, σ is a function defined by

$$\sigma(x)\equiv\frac{3}{x^3}\left\{1+x-\frac{1}{1+x}-2\log(1+x)\right\}$$

$$=3\left\{\frac{1}{3}-\frac{2}{4}x+\frac{3}{5}x^2-\frac{4}{6}x^3+\frac{5}{7}x^4\ldots.\right\} \quad . \quad (28)$$

and a is a certain average value in Å. for the closest distance of approach of two ions. If we regard all the ions as rigid spheres of the same size, then a is the diameter

of an ion in Å. The corresponding exact formula for the activity coefficient f_i of an ion i in water at 0° C. is

$$-\log_{10} f_i = 0{\cdot}486\, z_i^2\, \mathrm{I}^{1/2} \left\{ \frac{1}{1+\dfrac{a}{3{\cdot}08}\mathrm{I}^{1/2}} - \frac{V}{N_{H_2O}V_{H_2O} + \sum_k N_k V} \times \sum_k \frac{N_k z_k^2}{z_i^2}\, \sigma\left(\frac{\frac{a}{3{\cdot}08}\mathrm{I}^{1/2}}{3}\right) \right\}, \quad . \quad . \quad (29)$$

where the summation $\sum_k$ extends over all ionic species.

It can be shown that formulæ (28) and (29) satisfy the relation (7). Corresponding to (29) we have for the mean activity coefficient $f_\pm$ of an electrolyte whose molecule yields q_+ cations R of valency z_+ and q_- anions X of valency z_-

$$-\log_{10} f_{\mathrm{R,X}} = 0{\cdot}486\, z_+ \mid z_- \mid \mathrm{I}^{1/2} \frac{1}{1+\dfrac{a}{3{\cdot}08}\mathrm{I}^{1/2}} - 0{\cdot}486\, \frac{q_+V_R + q_-V_X}{N_{H_2O}V_{H_2O} + \sum_k N_k V_k} \sum_k \frac{N_k z_k^2}{q_+ + q_-}\, \sigma\left(\frac{\frac{a}{3{\cdot}08}\mathrm{I}^{1/2}}{3}\right). \quad . \quad . \quad . \quad (30)$$

These formulæ simplify considerably for solutions so dilute that $\sum_k N_k V_k$ is negligible compared with $N_{H_2O}\, V_{H_2O}$. Under these conditions we obtain

$$1-g = 0{\cdot}374\, \mathrm{I}^{1/2} \frac{\sum_i c_i z_i^2}{\sum_i c_i}\, \sigma\left(\frac{a}{3{\cdot}08}\mathrm{I}^{1/2}\right), \quad . \quad . \quad (31)$$

$$-\log_{10} f_i = 0{\cdot}486\, z_i^2 \mathrm{I}^{1/2} \frac{1}{1+\dfrac{a}{3{\cdot}08}\mathrm{I}^{1/2}}, \quad . \quad . \quad (32)$$

$$-\log_{10} f_\pm = 0{\cdot}486\, z_+ \mid z_- \mid \mathrm{I}^{1/2} \frac{1}{1+\dfrac{a}{3{\cdot}08}\mathrm{I}^{1/2}}. \quad . \quad . \quad (33)$$

Formulæ (31), (32), (33) are usually quoted as though they were the exact formulæ of the Debye-Hückel theory.

This is not the case, the exact formulæ being (26), (29), (30). The distinction is immaterial in dilute solutions, but must be remembered in case any attempt be made to extend the treatment to concentrated solutions. To obtain a rough estimate of the error due to the use of (31) instead of (26), let us assume that the partial molal volume V, of each ion is equal to V_{H_2O} that of the solvent water. In this case, for a solution of a binary electrolyte the fractional error in $1-g$ is equal to $\frac{z^2}{2}\Sigma N_i$. At an ionic strength 0·1 the error in $1-g$ is 1 in 500, that in g or in θ only 1 in 6000 for a uni-univalent electrolyte. The absolute error in θ is of the order of magnitude ·00005° C. This is slightly greater than the experimental uncertainty in a few of the best measurements, but is less than the uncertainty in the theoretical value of the coefficient 1·858 in formula (13) for the calculation of θ. The corresponding error in using (32) and (33) instead of (29) and (30) is for a uni-univalent electrolyte in decimolal solution only about one part in four thousand in f and so is quite negligible. We shall, therefore, for the sake of convenience, use the approximate formulæ (31), (32), (33), instead of the exact formulæ (26), (29), (30). The latter ought, however, to be used for the most accurate data as soon as a more accurate value becomes available for the coefficient 1·858 in formula (13).

Apart from variations in the value of a, the mean diameter of the ions, these formulæ would lead to activity coefficients of each electrolyte depending only on its electric type and on the total ionic strength of the solution. Such a behaviour was found to be roughly true by Lewis and Randall[26], and called the principle of ionic strength. It is, however, the individual specific properties of electrolytes, and so deviations from this principle with which we shall be chiefly concerned.

For a solution of a single electrolyte, formula (31) may be written

$$1-g=0{\cdot}374\,\mathrm{I}^{1/2}\,z_+\,|\,z_-\,|\,\sigma\Big(\frac{a}{3{\cdot}08}\,\mathrm{I}^{1/2}\Big). \quad . \quad . \quad (34)$$

If the electrolyte is symmetrical, this becomes

$$1-g=0{\cdot}374\,z^3c^{1/2}\sigma\Big(\frac{a}{3{\cdot}08}\,\mathrm{I}^{1/2}\Big). \quad . \quad . \quad . \quad (35)$$

In the limit of high dilutions σ tends towards unity and (35) takes the limiting form

$$1-g=0{\cdot}374\,z^3c^{1/2}, \quad . \quad . \quad . \quad . \quad . \quad (36)$$

of exactly the type as Milner's formula, and with a numerical coefficient intermediate between the two approximate values given by Milner's calculations. Thus, within the uncertainty due to Milner's numerical approximations, the two entirely different treatments of Milner on the one hand and of Debye and Hückel on the other lead to the same limiting laws at infinite dilution. The alleged discrepancy between the two theories does not exist.

3. *Limitations and Variations of the Debye-Hückel Treatment.*

The great mathematical simplicity of the treatment of Debye and Hückel, as contrasted with that of Milner, was achieved by two assumptions, either or both of which may be inaccurate. Firstly, instead of using the accurate principles of statistical mechanics as expounded by Gibbs, they applied the so-called Boltzmann formula to a set of conditions to which it is not strictly applicable. By combining this with the Poisson equation they obtained the differential equation usually referred to as the Poisson-Boltzmann formula, which forms the basis of their treatment. Secondly, in order to obtain a simple solution of this equation, they assumed that the mutual electrostatic potential energy of two ions at their closest distance of approach a is small compared with their mean thermal energy of translation. The first assumption has been analyzed by Onsager[32], who shows that it is equivalent to assuming that the potential of a given ion due to all the remaining ions is directly proportional to the charge of the given ion. The second assumption will be justifiable provided the ions are not too small. It so happens that in the solution obtained by Debye and Hückel the potential of a given ion due to the remaining ions does turn out to be proportional to its charge. Provided, then, that the ions are sufficiently large for the second assumption to be valid, their first assumption, though questionable, is consistent with their final result.

If, on the other hand, the ions are too small, the second assumption will lead to inaccurate results. In aqueous

solution the minimum value $a_{\text{min.}}$ of the closest distance of approach for which the second assumption is allowable is about $2z^3$ Å.; this is 2 Å. for univalent ions and 16 Å. for bivalent ions. Attempts have been made to improve the treatment of Debye and Hückel to deal with ions smaller than these values. No entirely accurate method has been found, but an approximate method of great ingenuity has been given by Bjerrum [4]. His treatment may be roughly described as follows. He divides the ions at any instant into two classes, those around which there is no other ion at a distance less than $a_{\text{min.}}$ and those which have another ion at a distance less than $a_{\text{min.}}$ He is able to calculate by the law of mass action what fraction of the ions belong to each class. He then applies the treatment of Debye and Hückel to each class separately, treating the ions of the first class as having a distance of closest approach of other ions equal to $a_{\text{min.}}$ (for if another ion comes closer than this it ceases to belong to the first class), and treating each ion-pair of the second class as if it were a single ion with a charge equal to the sum of those of the two ions which are at a distance less than $a_{\text{min.}}$ Bjerrum refers to such pairs of ions at a distance less than $a_{\text{min.}}$ as "associated ion-pairs," without, however, implying anything further than that the two ions are at that instant closer together than the distance $a_{\text{min.}}$ La Mer and other authors [11], in referring to Bjerrum's treatment, are wrong in implying that the conception of associated ion-pairs is an additional *ad hoc* physical assumption; it is nothing more than a convenient terminology. Other attempts to take account of small ions have been made by Müller [31] and by Gronwall [11]. Both these authors obtain numerical solutions without making the second assumption of Debye and Hückel, namely, that the mutual electrostatic energy of two ions at their closest distance of approach is small compared with their thermal energy, but both retain the first assumption, which is equivalent to assuming that the potential of a given ion due to the remaining ions is directly proportional to the charge of the given ion. Müller obtains a numerical solution by graphical integration, Gronwall by expansion in a power series of the charge of the ions. Their solutions agree satisfactorily with each other, but neither can be a strictly accurate solution of the problem; for they find that

the electric potential of a given ion due to the remaining ions is not simply proportional to the charge of the given ion, and this contradicts the first assumption of Debye and Hückel, which has been retained by both Müller and Gronwall.

To sum up, the treatment of Debye and Hückel may be satisfactory if the ions are not too small. If they are small it becomes inaccurate. The variations[4], [31], [11] of the theory to take account of small ions are all cumbersome, and none exact. Moreover, the treatment of the ions as rigid spheres of definite diameter is too crude a model to take account of the specific properties of various ions of the same valency. The interaction between them must depend not only on their sizes, but also on their shapes and polarizabilities. Another serious deficiency of the treatment of Debye and Hückel, and the above-mentioned variations of it, is their inability to take account of specific differences between several electrolytes of the same valence type in the same solution. In the formulæ there is only one variable parameter, the mean distance of closest approach of any two ions. It might be suggested that in a solution containing several kinds of ions independent values of a could be assigned to each ionic species, but this would conflict with thermodynamics, because the various activity coefficients are not independently variable, but are connected by relations of the type

$$\frac{\partial \log f_i}{\partial n_j} = \frac{\partial \log f_j}{\partial n_i} \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

The only quantitative treatment of the specific properties of various electrolytes in mixed solutions that has been at all satisfactory is due to Brönsted [5]. His theory of " specific interaction " is older than the theory of Debye and Hückel. Considering the strong experimental confirmation obtained by Brönsted for his theory, it is rather surprising that it has not been more widely used. It is our belief that the explanation is partly a difficulty of completely understanding the physical meaning of the theory of " specific interaction." The chief object of the present paper is to give a variant of Brönsted's theory, uniting it with that of Debye and Hückel and combining the useful features of both. We claim that the new treatment, as compared with that of Brönsted, is simpler, has a clearer physical basis, and is in equally good agreement

with experiment. As compared with that of Debye and Hückel it has the advantage of taking account of specific differences between several electrolytes of the same valence type in the same solution, and also of being more convenient to use from an arithmetical standpoint. It appears to be applicable to ions too small for the treatment of Debye and Hückel to be valid, and avoids the cumbersome numerical calculations of the treatments of Bjerrum[4], of Müller[31], and of Gronwall[11]. A preliminary account of this treatment, in so far as it applies to uni-univalent electrolytes, was given[15] in 1929. The publication of the present paper has been delayed so as to include a review of experimental data, especially those obtained by Scatchard, which has become available only recently.

4. *New Theory of Specific Thermodynamic Properties.*

In order to describe the thermodynamic properties of any solution of electrolytes it is convenient to compare it with a solution of the same concentration of standard electrolytes of the same valence type. As such standard, of each valence type, we might choose any one of the following alternatives :—

(1) An imaginary electrolyte whose ions obey some definite law of force, this being effectively Coulomb's law at all distances except very short ones, where we might, for example, assume a repulsive force varying inversely as some definite higher power of the distance.

(2) An imaginary electrolyte whose ions are rigid, perfectly impolarizable spheres of a certain given diameter.

(3) An imaginary electrolyte that accurately obeys the formulæ of Debye and Hückel, with some definite value assigned to the parameter a.

(4) Some one actual strong electrolyte.

The actual choice of a standard electrolyte is limited only by the condition that the interionic forces of actual electrolytes should differ from those of the standard electrolyte of the same valence type only for small interionic distances. For a great part of the ensuing argument it would not even be necessary to specify which of these standards we choose. However, for the

sake of definiteness and numerical convenience we choose the third alternative, with a value 3·08 assigned to the parameter a. The activity coefficient $f_{\pm}^{\text{stand.}}$ of the standard electrolyte of valence type (z_+, z_-) in water at 20° C. is then given by

$$\log_{10} f_{\pm}^{\text{stand.}} = -0{\cdot}50 \frac{z_+ \mid z_- \mid \mathrm{I}^{1/2}}{1+\mathrm{I}^{1/2}}, \quad . \quad . \quad (38)$$

a formula particularly simple to remember and use from a numerical point of view. At 0° C. the numerical coefficient 0·50 has the slightly lower value 0·486. The corresponding formula for the osmotic coefficient $g^{\text{stand.}}$ of a solution of the standard electrolyte of valence type (z_+, z_-) in water at 0° C. is

$$1-g^{\text{stand.}} = 0{\cdot}374\, z_+ \mid z_- \mid \mathrm{I}^{1/2}\sigma(\mathrm{I}^{1/2}). \quad . \quad . \quad (39)$$

In Table I. are given values of $\mathrm{I}^{1/2}$, of $\sigma(\mathrm{I}^{1/2})$, of $\log_{10} f_{\pm}^{\text{stand.}}/z_+ \mid z_- \mid$, and of $1-g^{\text{stand.}}/z_+ \mid z_- \mid$ for a given value of I.

If, now, we consider two actual ions of types α and β in some given relative configuration, their mutual potential energy $\mathrm{W}^{\alpha\beta}$ can be regarded as the sum of two terms

$$\mathrm{W}_{\alpha\beta} = \mathrm{W}_{\alpha\beta}^{\text{stand.}} + \mathrm{W}_{\alpha\beta}^{\text{spec.}}, \quad . \quad . \quad . \quad . \quad . \quad (40)$$

where $\mathrm{W}_{\alpha\beta}^{\text{stand.}}$ is the corresponding value for the two standard ions of the corresponding valency and $\mathrm{W}_{\alpha\beta}^{\text{spec.}}$ measures the specific deviations of the given ion pairs from the corresponding standard ion-pair. $\mathrm{W}_{\alpha\beta}^{\text{stand.}}$ is for all except small distances effectively the Coulomb energy, inversely proportional to the distance, being positive or negative according as the two ions α and β are of the same or opposite sign. $\mathrm{W}_{\alpha\beta}^{\text{spec.}}$, on the other hand, is for all except small distances between the two ions effectively zero, for only at small distances do the specific differences between the ions α, β and the corresponding standard ions become sensible. We shall now assume as an approximation that the contributions of $\mathrm{W}_{\alpha\beta}^{\text{stand.}}$ and $\mathrm{W}_{\alpha\beta}^{\text{spec.}}$ to the thermodynamic functions are additive. This assumption will not be exact, but might be expected to be reasonably accurate provided the contribution of $\mathrm{W}_{\alpha\beta}^{\text{spec.}}$ is small compared with that of $\mathrm{W}_{\alpha\beta}^{\text{stand.}}$. The contribution $\mathrm{G}^{\text{int.}}$ of the interionic energy to the thermodynamic potential G may then also be split into two parts,

$$\mathrm{G}^{\text{int.}} = \mathrm{G}^{\text{stand.}} + \mathrm{G}^{\text{spec.}}, \quad . \quad . \quad . \quad . \quad . \quad (41)$$

where $G^{\text{stand.}}$ is the corresponding contribution in the standard solution and $G^{\text{spec.}}$ is the contribution due to the specific part $W_{\alpha\beta}^{\text{spec.}}$ of the interionic energy. Now $W_{\alpha\beta}^{\text{spec.}}$ will be an extremely complicated function of the sizes, shapes, electron configuration, polarizabilities, and

TABLE I.

I.	$I^{1/2}$.	$\sigma(I^{1/2})$.	$\frac{1-g^{\text{stand}}}{\epsilon_+\lvert\epsilon_-\rvert}$.	$\frac{-\log_{10} f_{\pm}^{\text{stand.}}}{\epsilon_+\lvert\epsilon_-\rvert}$.
·001	·0316	·954	·0113	·0153
·002	·0447	·936	·0156	·0214
·005	·0707	·902	·0238	·0330
·006	·0775	·893	·0259	·0360
·007	·0837	·886	·0277	·0386
·008	·0894	·879	·0294	·0411
·009	·0949	·871	·0309	·0433
·010	·1000	·866*	·0323	·0455
·020	·1414	·818	·0433	·0619
·030	·1732	·786	·0509	·0738
·040	·2000	·759	·0568	·0833
·050	·2236	·738	·0617	·0913
·060	·2449	·717	·0657	·0985
·070	·2646	·700	·0693	·1047
·080	·2828	·685	·0725	·1102
·090	·3000	·671	·0753	·1154
·100	·3162	·659	·0781	·1202
·110	·3317	·646	·0802	·1244
·120	·3464	·636	·0824	·1287
·150	·3873	·607	·0880	·1396
·200	·4472	·569	·0952	·1545

* This value is erroneously given as ·855 by Debye and Hückel[9].

relative positions of the two ions α and β. The complicated nature of $W_{\alpha\beta}^{\text{spec.}}$, however, does not matter, because the energy involved is due to typical "short-range" forces, that is to say, it is negligible except at distances of molecular dimensions. Hence, according to well-known statistical mechanical reasoning, the contribution

of $W_{\alpha\beta}^{spec.}$ to the thermodynamic potential per unit volume of the solution is proportional to the product of the concentrations of α and β. In fact $G_{\beta}^{spec.}$ is given by the formula

$$G^{spec.} = \frac{1}{V} \sum_{\alpha\beta} n_{\alpha} n_{\beta} v_{\alpha\beta} \quad . \quad . \quad . \quad . \quad . \quad (42)$$

where V is the volume of the solution and n_{α}, n_{β} the number of gram-ions of types α and β.

Finally, $v_{\alpha\beta}$ is defined by [10]

$$v_{\alpha\beta} = RT \int \left(1 - e^{-W_{\alpha\beta}^{spec.}/kT}\right) d\omega, \quad . \quad . \quad (43)$$

where $d\omega$ denotes the element of volume occupied by the β-ion defined relatively to the α-ion, and the integral extends over all relative configurations of the two ions. The only relative configurations whose contributions to the integral differ appreciably from zero are those in which the two ions are very near each other, since for all other relative configurations $W_{\alpha\beta}^{spec.}$ is effectively zero, so that $1 - e^{-W_{\alpha\beta}^{spec.}/kT}$ is also effectively zero. To be precise $W_{\alpha\beta}^{spec.}$ occurring in (43) is a certain average value for all possible orientations of the α- and β-ions for given relative positions of their centres of mass. $v_{\alpha\beta}$ is therefore, like $W_{\alpha\beta}^{spec.}$, a complicated function of the specific properties of the α- and β-ions. It will also depend on the temperature and nature of the solvent, but is independent of the concentrations of the various solute species. Thus for a given solvent and temperature the $v_{\alpha\beta}$ may be considered as constants characteristic of each type of ion-pair. We now make use of the fundamental principle underlying Brönsted's theory of the "specific interaction of ions." This principle is that, owing to the repulsive forces between two ions of the same sign, they will rarely approach each other sufficiently closely for their individual characteristic structures to make themselves felt. In Brönsted's words [5], "ions are uniformly influenced by ions of their own sign, and specifically influenced only by ions of opposite sign." According to this assumption we may take $v_{\alpha\beta}$ to be zero for the case that α and β have the same sign. We therefore write

$$G^{spec.} = \frac{1}{V} \sum_{R,X} n_R n_X v_{R,X} \quad . \quad . \quad . \quad . \quad (44)$$

where R denotes any cation and X any anion. There are, therefore, for given temperature and solvent as many characteristic constants $\nu_{R,X}$ as there are single electrolytes of the given valence type. Formula (44) thus defines the thermodynamic properties of any solution containing a mixture of electrolytes in terms of the thermodynamic properties of solutions of the separate single electrolytes.

The whole of the present theory is contained in (44). Before we investigate what conclusions can be drawn from it, it will be well to state clearly on what assumptions it is based. The first assumption is that the specific effects of ions on one another are negligible except at short distances. The second is that the interaction corresponding to the standard electrolyte and the specific interaction corresponding to divergence from the standard electrolyte contribute additively to the thermodynamic potential. The third is that we need consider specific interaction of ion-pairs only, and may ignore simultaneous triplet interaction. This assumption will certainly be fulfilled as long as the solution is sufficiently dilute. The fourth, and most important, assumption is that of Brönsted, that we need to take account of specific interaction only between ions of opposite sign.

Applying a similar notation to that of (41) to the mean activity coefficient $f_{R,X}$ of an electrolyte (R, X) with cation R and anion X,

$$\log f_{R,X} = \log f_{\pm}^{\text{stand.}} + \log f_{R,X}^{\text{spec.}} \quad . \quad . \quad . \quad (45)$$

or

$$f_{R,X} = f_{\pm}^{\text{stand.}} \cdot f_{R,X}^{\text{spec.}}, \quad . \quad . \quad . \quad . \quad . \quad (46)$$

where $f_{\pm}^{\text{stand.}}$ denotes the mean activity coefficient of the standard electrolyte of the same valence type at the same total ion concentration and $f_{R,X}^{\text{spec.}}$ is the ratio of the mean activity coefficient of (R, X) to that of the standard electrolyte at the same total ion concentration. According to the definition of the mean activity coefficient $f_{R,X}$ of an electrolyte whose molecule gives q_+ cations R of valency z_+, and q_- anions X of valency z_-,

$$(q_+ + q_-)RT \log f_{R,X}^{\text{spec.}} = q_+ \frac{\partial G^{\text{spec.}}}{\partial n_R} + q_- \frac{\partial G^{\text{spec.}}}{\partial n_X} \quad . \quad . \quad (47)$$

Substituting from (44) into (47) we obtain

$$(q_+ + q_-)\mathrm{RT}\log f^{\mathrm{spec.}}_{\mathrm{R,X}} = q_+ \sum_{\mathrm{X}'} \frac{n_{\mathrm{X}'}}{V} v_{\mathrm{R,X}'} + q_- \sum_{\mathrm{R}'} \frac{n_{\mathrm{R}'}}{V} v_{\mathrm{R}',\mathrm{X}}. \quad . \quad . \quad . \quad (48)$$

Introducing the volume concentrations c defined by

$$c_i = \frac{n_i}{V}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (49)$$

and using the substitution

$$\lambda_{\mathrm{R,X}} = \frac{v_{\mathrm{R,X}}}{\mathrm{RT}\log_e 10}, \quad . \quad . \quad . \quad . \quad . \quad (50)$$

we obtain

$$\log_{10} f^{\mathrm{spec.}}_{\mathrm{R,X}} = \frac{q_+}{q_+ + q_-} \sum_{\mathrm{X}'} \lambda_{\mathrm{R,X}'} c_{\mathrm{X}'} + \frac{q_-}{q_+ + q_-} \sum_{\mathrm{R}'} \lambda_{\mathrm{R}',\mathrm{X}} c_{\mathrm{R}'}, \quad . \quad (51)$$

where the $\lambda_{\mathrm{R,X}}$, like the $v_{\mathrm{R,X}}$, are for the given temperature and solvent, characteristic constants of the various single electrolytes. Using (38) for $f^{\mathrm{stand.}}_{\pm}$ we obtain, finally, for the mean activity coefficient $f_{\mathrm{R,X}}$

$$\log_{10} f_{\mathrm{R,X}} = -0{\cdot}50 \frac{z_+ \mid z_- \mid \mathrm{I}^{1/2}}{1 + \mathrm{I}^{1/2}} + \frac{q_+}{q_+ + q_-} \sum_{\mathrm{X}'} \lambda_{\mathrm{R,X}'} c_{\mathrm{X}'} + \frac{q_-}{q_+ + q_-} \sum_{\mathrm{R}'} \lambda_{\mathrm{R}',\mathrm{X}} c_{\mathrm{R}'}. \quad . \quad . \quad (52)$$

For a symmetrical electrolyte of valence type $(z,-z)$ formula (52) simplifies to

$$\log_{10} f_{\mathrm{R,X}} = -0{\cdot}50 \frac{z^2 \mathrm{I}^{1/2}}{1 + \mathrm{I}^{1/2}} + \tfrac{1}{2} \sum_{\mathrm{X}'} \lambda_{\mathrm{R,X}'} c_{\mathrm{X}'} + \tfrac{1}{2} \sum_{\mathrm{R}'} \lambda_{\mathrm{R}',\mathrm{X}} c_{\mathrm{R}'}. \quad . \quad . \quad (53)$$

For the special case that all the electrolytes in the solution are of the same valence type $(z_+\ z_-)$ it is convenient to describe the relative composition by means of the fractions x_{R}, x_{X}, defined by

$$c_{\mathrm{R}} = x_{\mathrm{R}} \sum_{\mathrm{R}'} c_{\mathrm{R}'} = x_{\mathrm{R}} q_+ \mathrm{C}, \quad . \quad . \quad . \quad . \quad (54)$$

$$c_{\mathrm{X}} = x_{\mathrm{X}} \sum_{\mathrm{X}'} c_{\mathrm{X}'} = x_{\mathrm{X}} q_- \mathrm{C}, \quad . \quad . \quad . \quad . \quad (55)$$

where C is the total molar concentration, given by

$$C = \frac{\sum_{\mathrm{R}} c_{\mathrm{R}}}{q_+} + \frac{\sum_{\mathrm{X}} c_{\mathrm{X}}}{q_-} \quad . \quad . \quad . \quad . \quad . \quad . \quad (56)$$

In this case formula (52) can be written in the alternative form—

$$\left.\begin{aligned}\log_{10} f_{\mathrm{R,X}} &= -0{\cdot}50\, z_+ \mid z_- \mid \frac{\mathrm{I}^{1/2}}{1+\mathrm{I}^{1/2}} + C\,\frac{q_+ q_-}{q_+ + q_-}\left\{\sum_{\mathrm{X}'}\lambda_{\mathrm{R,X}'}\, x_{\mathrm{X}'} + \sum_{\mathrm{R}'}\lambda_{\mathrm{R}',\mathrm{X}}\, x_{\mathrm{R}'}\right\} \\ &= -0{\cdot}50\, z_+ \mid z_- \mid \frac{\mathrm{I}^{1/2}}{1+\mathrm{I}^{1/2}} + \tfrac{1}{2}Cq\left\{\sum_{\mathrm{X}'}\lambda_{\mathrm{R,X}'}\, x_{\mathrm{X}'} + \sum_{\mathrm{R}'}\lambda_{\mathrm{R}',\mathrm{X}}\, x_{\mathrm{R}'}\right\}\end{aligned}\right\}, \quad . \quad . \quad . \quad (57)$$

where q is the harmonic mean of q_+ and q_-, defined by

$$\frac{2}{q} = \frac{1}{q_+} + \frac{1}{q_-} \quad . \quad . \quad . \quad . \quad . \quad . \quad (58)$$

By means of the electroneutrality condition

$$q_+ z_+ = -q_- z_- = q_- \mid z_- \mid \quad . \quad . \quad . \quad . \quad (59)$$

we can transform (57) to

$$\log_{10} f_{\mathrm{R,X}} = -0{\cdot}50\, \frac{z_+ \mid z_- \mid \mathrm{I}^{1/2}}{1+\mathrm{I}^{1/2}} + \frac{1}{2z^2}\left\{\sum_{\mathrm{X}'}\lambda_{\mathrm{R,X}'} x_{\mathrm{X}'} + \sum_{\mathrm{R}'}\lambda_{\mathrm{R}',\mathrm{X}} x_{\mathrm{R}'}\right\}, \quad . \quad . \quad . \quad (60)$$

where z is the arithmetic mean of z_+ and $\mid z_- \mid$, defined by

$$2z = z_+ + \mid z_- \mid . \quad . \quad . \quad . \quad . \quad (61)$$

By making use of the relation (18) it is easy to deduce corresponding formulæ for the osmotic coefficient $1-g$ of the solution. In the case that all the electrolytes in the solution are of the same valence type we obtain

$$\left.\begin{aligned}1-g &= 0{\cdot}374\, z_+ \mid z_- \mid \mathrm{I}^{1/2}\sigma(\mathrm{I}^{1/2}) - \frac{2{\cdot}30}{2} Cq \sum_{\mathrm{R}}\sum_{\mathrm{X}}\lambda_{\mathrm{R,X}} x_{\mathrm{R}} x_{\mathrm{X}} \\ &= 0{\cdot}374\, z_+ \mid z_- \mid \mathrm{I}^{1/2}\sigma(\mathrm{I}^{1/2}) - \frac{2{\cdot}30\,\mathrm{I}}{2z^2}\sum_{\mathrm{R}}\sum_{\mathrm{X}}\lambda_{\mathrm{R,X}} x_{\mathrm{R}} x_{\mathrm{X}}.\end{aligned}\right\} \quad . \quad . \quad . \quad (62)$$

From these formulæ we can draw a number of general conclusions which can be verified experimentally.

5. *Range of Applicability of Theory.*

The concentration range where the present theory may be expected to be accurate and useful is that in which specific differences between different electrolytes of the same valence type are appreciable but not overwhelming. The concentration must also be sufficiently low to justify our ignoring triplet interaction. Measurements in the range of ionic strengths up to about 0·1 are, therefore, most suitable. We claim that for solutions of single electrolytes our formulæ with one variable parameter λ represent the data in these dilute solutions at least as well as the formulæ of Debye and Hückel with the one variable parameter a. Our formulæ have the advantage over those of Debye and Hückel that they automatically take account of the specific differences between individual electrolytes in a mixed solution without the introduction of any new parameters.

Naturally a fit over a longer range of concentrations could be obtained by using a formula such as

$$\log_{10} f_{\pm} = -0{\cdot}50\, z_+ \mid z_- \mid \frac{\mathrm{I}^{1/2}}{1+\dfrac{a}{3{\cdot}08}\mathrm{I}^{1/2}} + \mathrm{BI}, \quad . \quad . \quad . \quad (63)$$

with two adjustable parameters a and B. As a matter of fact the data for HCl at 20° C. are fitted by the formula [18]

$$\log_{10} \gamma_{\mathrm{II,\,Cl}} = -\frac{0{\cdot}50\,\mathrm{C}^{1/2}}{1+1{\cdot}40\,\mathrm{C}^{1/2}} + 0{\cdot}136\,\mathrm{C} \quad . \quad . \quad (64)$$

at concentrations extending right up to 1·0 molal. Hückel [23] has pointed out that a term linear in the ionic strength will occur on account of the variation of the dielectric constant with the concentration. If, however, we were to interpret formula (64) as corresponding to an ionic diameter 4·2 Å., and attribute the term linear in C as due entirely to the change in dielectric constant, we should find [18] that at high concentrations this corresponded to attributing a negative value to the dielectric constant, which is absurd. It is fairly obvious that several other causes, as well as variation of the dielectric constant, may contribute to the term linear in the concentration.

Amongst such causes is interaction between solute ions and solvent, which, if strong, may be thought of as solvation of the solute ions. A second such cause is short-range force interaction between the solute ions, that is to say, deviations from Coulomb's law at short distances; this may be due partly to deviations from spherical symmetry of the ions and partly to mutual polarization. A third possible cause is incomplete dissociation at high concentrations. Whereas all the evidence points to effectively complete dissociation of most strong electrolytes in aqueous solution at concentrations up to about tenth molar, there is no convincing evidence either for or against the persistence of this state of affairs in concentrated solution. It is obviously impossible to separate these various factors merely by a study of the thermodynamic properties of an electrolyte solution, since they all contribute in a similar manner to the activity coefficient. Since, moreover, the denominator $1+\frac{a}{3{\cdot}08}C^{1/2}$ in (63) as a first approximation also gives a contribution linear in the concentration, it is unsafe to assume that the value of the parameter a, which gives the best fit in (63), is really a measure of the mean ionic diameter. In short, the most valuable feature of the theory of Debye and Hückel is that it gives the general type of formula for the activity coefficient. All the evidence, both theoretical and experimental, is in favour of the correctness of the limiting law at infinite dilution,

$$\log_{10} f_{\pm} = -0{\cdot}50\, z_+ \mid z_- \mid I^{1/2}. \quad . \quad . \quad . \quad (65)$$

If, then, in computing activity coefficients from experimental data, we can obtain a good fit over the whole concentration range by means of a formula of the type (60) or (63), we can feel reasonably safe that the extrapolation to infinite dilution is correct. On the other hand, the parameter a in (63) will not necessarily be an accurate value of the mean ionic diameter, and the parameters λ in (60) and B in (63) will be purely empirical. Another disadvantage of formulæ of the type (33) and (63) is the impossibility of extending them to mixtures if the value of a is different for the several electrolytes, owing to the thermodynamic restriction (37).

We wish to emphasize that the formulæ of the present

theory are applicable only to dilute solutions. An extension to concentrated solutions would require more than one parameter for each single electrolyte.

6. *Application to Solutions of Single Electrolytes.*

From (57) we obtain for the activity coefficient $f^{\mathrm{R,X}}_{\mathrm{R,X}}$ of an electrolyte composed of the ions R and X in a solution containing no other electrolyte,

$$\left.\begin{aligned}\log_{10} f^{\mathrm{R,X}}_{\mathrm{R,X}} &= -0{\cdot}50\,\frac{z_+ \mid z_- \mid \mathrm{I}^{1/2}}{1+\mathrm{I}^{1/2}} + Cq\lambda_{\mathrm{R,X}} \\ &= -0{\cdot}50\,\frac{z_+ \mid z_- \mid \mathrm{I}^{1/2}}{1+\mathrm{I}^{1/2}} + \frac{\mathrm{I}}{z^2}\lambda_{\mathrm{R,X}}\end{aligned}\right\} . \quad (66)$$

Thus the interaction coefficient $\lambda_{\mathrm{R,X}}$ is directly determinable by measuring the mean activity coefficient of the electrolyte (R, X) at one concentration. If, then, our theory is correct, one such determination for each single electrolyte will make it possible to calculate the activity coefficient of any electrolyte in any mixture. Alternatively, from (62) we obtain for the osmotic coefficient g of a solution of a single electrolyte

$$\left.\begin{aligned}1-g &= 0{\cdot}374\, z_+ \mid z_- \mid \mathrm{I}^{1/2}\sigma(\mathrm{I}^{1/2}) + \frac{2{\cdot}30}{2}Cq\,\lambda_{\mathrm{R,X}} \\ &= 0{\cdot}374\, z_+ \mid z_- \mid \mathrm{I}^{1/2}\sigma(\mathrm{I}^{1/2}) + \frac{2{\cdot}30}{2}\frac{\mathrm{I}}{z^2}\lambda_{\mathrm{R,X}}\end{aligned}\right\} . \quad (67)$$

so that each $\lambda_{\mathrm{R,X}}$ may be determined by a single freezing-point measurement on each single electrolyte.

Before applying our formulæ to mixtures (their really useful application) it is important to test their accuracy when applied to solutions of single electrolytes. Data of high accuracy are required, as differences between electrolytes of the same valence type are comparatively small in the dilute solutions where the theory is applicable.

The most suitable data are freezing-point measurements, and we shall consider in detail the available experimental material. The logical way to test the applicability of formula (67) to a given single electrolyte is to examine whether, by assigning a suitable value to $\lambda_{\mathrm{R,X}}$, we can obtain theoretical values $\theta_{\mathrm{theor.}}$ for the freezing-point lowerings agreeing with the observed values $\theta_{\mathrm{expl.}}$ within the limits of the experimental accuracy. This is more rational

than comparing theoretical and observed values of the osmotic coefficient g, because a very small experimental error in the freezing-point lowering θ will, *at the lowest concentrations*, produce a large error in g, since the observed value $g_{exp.}$ is calculated from

$$g_{exp.} = \frac{\theta_{exp.}}{\theta_{ideal.}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (68)$$

An even more irrational method of testing a theoretical formula is that used by Randall[36]. From the experimental data he obtains values of ϕ, and then, by extrapolation to infinite dilution and use of the formula (10), he computes values of $\gamma_{\pm}$. He then compares these so-called experimental vaules with the theoretical values, apparently failing to realize that he has used an extrapolation which itself contradicts the theoretical formulæ. The discrepancy reported by Randall and Vanselow[36] between their freezing-point data for HCl and the formulæ of Debye and Hückel is, at concentrations below 0·01 M, due entirely to their having used an extrapolation which contradicts the theory which they are supposed to be testing.

In Table II. is given a list of the values which we have assigned to the interaction coefficients $\lambda_{R,X}$ to fit the best available freezing-point data and a list of the sources of these data. In the subsequent tables is given a comparison between the experimental data and the theoretical values of the freezing-point lowering corresponding to the λ values given in Table II. In each case the values of θ_{ideal} are calculated according to the formula

$$\left.\begin{aligned} \theta_{ideal} &= 1{\cdot}858 \times \frac{1000}{18} \log (1 - N_R - Nx) \\ &= 1{\cdot}858 \times \frac{1000}{18} \log \left\{ 1 - \frac{(q_+ + q_-)m}{\frac{1000}{18} + (q_+ + q_-)m} \right\} \\ &= 1{\cdot}858\,(q_+ + q_-)m \left\{ 1 + 0{\cdot}0018 \frac{q_+ + q_-}{2} m \right\}, \end{aligned}\right\} \quad . \quad (69)$$

terms of the order m^3 being neglected. The theoretical value of the freezing-point depression is then calculated from the theoretical value $g_{theor.}$ of the osmotic coefficients by means of the relation

$$\theta_{theor.} = \theta_{ideal} - (1 - g_{theor.})\theta_{ideal}, \quad . \quad . \quad . \quad (70)$$

and this value is compared with the experimental value $\theta_{\text{exp.}}$. It appears that the agreement between $\theta_{\text{theor.}}$ and $\theta_{\text{exp.}}$ is almost invariably within the probable experimental error.

Table II.

Values of λ fitting freezing-point data of single electrolytes in formula for osmotic coefficient:

$$1-g=0{\cdot}374\, z_+ \mid z_- \mid \mathrm{I}^{1/2}\sigma(\mathrm{I}^{1/2})-\frac{2{\cdot}30}{2}q\lambda\mathrm{C}.$$

The corresponding formula for the mean activity coefficient of single electrolyte is

$$\log_{10} f_{\pm}=-0{\cdot}486\,\frac{z_+ \mid z_- \mid \mathrm{I}^{1/2}}{1+\mathrm{I}^{1/2}}+q\lambda\mathrm{C}.$$

Electrolyte.	q.	λ.	$q\lambda$.	$\frac{2{\cdot}30}{2}q\lambda$.	Authors.
HCl	1	+·240	+·240	+·275	Randall and Vanselow [36].
LiCl	1	+·195	+·195	+·225	Scatchard and Prentiss [39].
NaCl	1	+·117	+·117	+·135	Scatchard and Prentiss [39]; Harkins and Roberts [20].
KCl	1	+·056	+·056	+·065	Scatchard and Prentiss [39].
		+·072	+·072	+·083	Adams [1]; Hovorka and Rodebush [22].
TlCl	1	+·35	+·35	+·40	Randall and Vanselow [36].
$LiNO_3$	1	+·23	+·23	+·26	Scatchard, Jones, and Prentiss [38].
$NaNO_3$	1	·00	·00	·00	Scatchard, Jones, and Prentiss [38].
KNO_3	1	−·21	−·21	−·24	Scatchard, Jones and Prentiss [38].
		−·25	−·25	−·29	Adams [1].
$CsNO_3$	1	·00	·00	·00	Hovorka and Rodobush [22].
$NaIO_3$	1	−·35	−·35	−·40	Hall and Harkins [19].
KIO_3.....	1	−·35	−·35	−·40	Hall and Harkins [19].
Na_2SO_4	4/3	−·39	−·52	−·60	Randall and Scott [35].
K_2SO_4	4/3	·00	·00	·00	Hall and Harkins [19]; Hovorka and Rodebush [22].

TABLE II. (*cont.*).

Electrolyte.	q.	λ.	$q\lambda$.	$\frac{2{\cdot}30}{2}q\lambda$.	Authors.
$Ba(NO_3)_2$	4/3	−·36	−·48	−·55	Randall and Scott[35]; Hovorka and Rodebush[22].
$MgSO_4$	1	·00	·00	·00	Hall and Harkins[19]; Hovorka and Rodebush[22].
$CuSO_4$	1	−1·5	−1·5	−1·7	Hovorka and Rodebush[23].
$La(NO_3)_3$	3/2	+2·25	+3·4	+3·9	Hall and Harkins[19].
$La_2(SO_4)_3$ ..	12/5	·00	·00	·00	Hovorka and Rodebush[23].

TABLE III.

Freezing-point data of Randall and Vanselow[36] for HCl :

$$1-g=0{\cdot}374\,C^{1/2}\sigma(C^{1/2})-0{\cdot}275\,C.$$

Molality (moles /1000 g. H_2O).	$C^{1/2}$.	$1-g_{theor.}$	$\theta_{ideal.}$	$\theta_{theor.}$	$\theta_{exp.}$	$\theta_{exp.}-\theta_{theor.}$
·000027	·0250	·0088	·00233	·00231	·00228	−·00003
·001179	·0343	·0118	·00438	·00433	·00434	+·00001
·001245	·0353	·0121	·00463	·00457	·00455	−·00002
·001474	·0384	·0131	·00548	·00541	·00542	+·00001
·001821	·0427	·0144	·00677	·00667	·00668	+·00001
·001887	·0434	·0146	·00701	·00691	·00693	+·00002
·002228	·0472	·0158	·00828	·00815	·00815	·00000
·002403	·0491	·0163	·00893	·00879	·00880	+·00001
·003430	·0586	·0192	·01275	·01251	·01253	+·00002
·003526	·0594	·0194	·01310	·01285	·01286	+·00001
·003719	·0610	·0198	·01382	·01355	·01358	+·00003
·004520	·0672	·0216	·01680	·01644	·01644	·00000
·004822	·0694	·0222	·01791	·01751	·01755	+·00004
·005210	·0722	·0230	·01937	·01892	·01892	·00000
·006879	·0829	·0256	·02556	·02491	·02494	+·00003
·008329	·0912	·0277	·03095	·03009	·03011	+·00002
·008573	·0926	·0280	·03185	·03096	·03097	+·00001

TABLE III. (*cont.*).

Molality (moles /1000 g. H_2O).	$C^{1/2}$.	$1=g_{theor.}$	θ_{ideal}	$\theta_{theor.}$	$\theta_{exp.}$	$\theta_{exp.}-\theta_{theor.}$
·010633	·1031	·0304	·03950	·03830	·03848	+·00018
·013258	·1151	·0327	·04926	·04765	·04763	−·00002
·017379	·1318	·0353	·06456	·06228	·06211	−·00017
·027439	·1655	·04195	·10191	·09764	·09746	−·00018
·044012	·2096	·0469	·16342	·15574	·15567	−·00007
·050063	·2235	·0482	·18587	·17692	·1774	+·0005*
·051633	·2270	·0485	·19169	·1824	·1828	+·0004*
·067072	·2587	·0499	·24894	·2364	·2364	·0000
·070576	·2653	·0501	·26193	·2488	·2489	+·0001
·104591	·3229	·0501	·38793	·3683	·3684	+·0001

* A large-scale plot of the experimental data shows that these two points cannot lie on any smooth curve agreeing with the remaining points.

TABLE IV.

Freezing-point data of Scatchard and Prentiss[39] for LiCl :

$$1-g=0{\cdot}374\ C^{1/2}\sigma(C^{1/2})-0{\cdot}225\ C.$$

Molality, m.	$C^{1/2}$.	$1-g_{theor.}$	$1-\phi_{exp.}$	$1-g_{exp.}$	$\theta_{exp.}-\theta_{theor.}$
·000815	·0284	·010	·0125	·0125	−·00001
·001000	·0314	·011	·0369	·0369	−·00015
·001388	·0371	·013	·0246	·0246	−·00009
·001889	·0433	·0150	·0215	·0215	−·00006
·003350	·0576	·0190	·0263	·0263	−·00015
·003706	·0606	·0207	·0233	·0233	−·00007
·005982	·0770	·0242	·0264	·0263	−·00007
·010810	·1033	·0322	·0334	·0332	−·00006
·017113	·130	·0370	·0393	·0390	−·0002
·028830	·169	·0439	·0442	·0437	+·00003
·041929	·204	·0486	·0484	·0477	+·0002
·062321	·248	·0528	·0534	·0522	+·0003
·083317	·287	·0548	·0552	·0538	+·0005
·10807	·327	·0557	·0573	·0556	+·00006
·13317	·363	·0551	·0577	·0554	−·0002

TABLE V. A.

Freezing-point data of Scatchard and Prentiss[39] for NaCl:

$$1-g=0{\cdot}374\,C^{1/2}\sigma(C^{1/2})-0{\cdot}135\,C.$$

Molality, m.	$C^{1/2}$.	$1-g_{theor.}$	$1-\phi_{exp.}$	$1-g_{exp.}$	$\theta_{exp.}-\theta_{theor.}$
·000819	·0284	·0102	−·0092	−·0092	+·0001
·001866	·0430	·0145	·0092	·0092	+·00005
·005120	·0712	·0233	·0192	·0192	+·0001
·008605	·0924	·0294	·0265	·0264	+·0002
·013540	·1155	·0347	·0334	·0332	+·0002
·022648	·1498	·0427	·0445	·0441	−·0001
·033489	·1820	·0488	·0468	·0462	+·0003
·054924	·233	·0561	·0553	·0544	+·0011
·078838	·279	·0605	·0628	·0615	−·0012
·10371	·320	·0651	·0668	·0651	·0000
·12579	·352	·0666	·0710	·0689	−·0040

TABLE V. B.

Freezing-point data of Harkins and Roberts[20] on NaCl:

$$1-g=0{\cdot}374\,C^{1/2}\sigma(C^{1/2})-0{\cdot}135\,C.$$

Molality, m.	$C^{1/2}$.	$1-g_{theor.}$	$1-\phi_{exp.}$	$1-g_{exp.}$	$\theta_{exp.}-\theta_{theor.}$
·005132	·072	·023	·018	·018	+·0001
·009544	·098	·031	·025	·025	+·0002
·009604	·098	·031	·027	·027	+·00015
·02012	·142	·041	·0417	·0415	−·00004
·02120	·146	·042	·0420	·0417	+·00002
·03516	·188	·050	·0490	·0485	+·0002
·06534	·256	·059	·0586	·0575	+·0003
·08360	·289	·063	·0757	·0743	−·0035*
·1360	·369	·068	·0722	·0695	−·0007

* A large-scale plot of the data shows conclusively that this experimental point is greatly in error.

TABLE VI. A.

Freezing-point data of Scatchard and Prentiss[39] on KCl :

$$1-g=0{\cdot}374\,C^{1/2}\sigma(C^{1/2})-0{\cdot}065\,C.$$

Molality, m.	$C^{1/2}$.	$1-g_{\text{theor.}}$	$1-\phi_{\text{exp.}}$	$1-g_{\text{exp.}}$	$\theta_{\text{exp.}}-\theta_{\text{theor.}}$
·001389	·0371	·013	·0044	·0044	·0000
·002865	·0533	·018	·0344	·0344	−·00016
·006449	·0800	·026	·0235	·0234	+·0001
·011136	·1050	·033	·0353	·0351	·0000
·016217	·1267	·0390	·0371	·0368	+·00023
·027000	·1634	·0470	·0462	·0457	+·00021
·038173	·1942	·0528	·0537	·0531	−·0001
·056239	·2360	·0608	·0593	·0583	+·0005
·076739	·2755	·0666	·0675	·0662	+·00018
·10646	·325	·0723	·0742	·0724	−·00006

TABLE VI. B.

Freezing-point measurements of Adams[1] on KCl :

$$1-g=0{\cdot}374\,C^{1/2}\sigma(C^{1/2})-0{\cdot}083\,C.$$

Molality, m.	$C^{1/2}$.	$1-g_{\text{theor.}}$	$\theta_{\text{ideal.}}$	$\theta_{\text{theor.}}$	$\theta_{\text{exp.}}$	$\theta_{\text{exp.}}-\theta_{\text{theor.}}$
·00506	·071	·024	·01880	·01835	·0184	+·00005
·00963	·098	·031	·03579	·0347	·0348	+·0001
·01648	·128	·039	·06134	·0589	·0590	+·0001
·03170	·178	·049	·11772	·1120	·1122	+·0002
·05818	·241	·061	·21597	·2028	·2031	+·0003
·11679	·342	·073	·43310	·4015	·4014	−·0001

TABLE VI. c.

Freezing-point measurements of Hovorka and Rodebush[22] on KCl:

$$1-g=0{\cdot}374\ C^{1/2}\sigma(C^{1/2})-0{\cdot}083\ C.$$

Molality, m.	$C^{1/2}$.	$1-g_{theor.}$	$\theta_{ideal.}$	$\theta_{theor.}$	$\theta_{exp.}$	$\theta_{exp.}-\theta_{theor.}$
·001	·0316	·0111	·00372	·00368	·00368	·00000
					·00363	−·00005
					·00365	−·00003
·005	·0706	·0235	·01858	·01814	·01818	+·00004
					·01822	+·00008
·010	·1000	·0316	·03716	·03599	·03610	+·00011
					·03590	−·00009

TABLE VII.

Freezing-point data of Randall and Vanselow[36] on TlCl:

$$1-g=0{\cdot}374\ C^{1/2}\sigma(C^{1/2})-0{\cdot}40\ C.$$

Molality, m.	$C^{1/2}$.	$1-g_{theor.}$	$\theta_{ideal.}$	$\theta_{theor.}$	$\theta_{exp.}$	$\theta_{exp.}-\theta_{theor.}$
·000473	·0218	·0077	·00176	·001745	·00174	·00000
·000862	·0294	·01005	·00320	·00317	·00318	+·00001
·000877	·0296	·01015	·00326	·00323	·00322	−·00001
·001057	·0324	·0111	·00393	·00389	·003885	·00000
·001305	·0361	·0122	·00485	·00479	·00480	+·00001
·001349	·0368	·0125	·00501	·00495	·00498	+·00003
·001602	·0400	·01335	·00595	·00587	·00588	+·00001
·001973	·0444	·0147	·00733	·00722	·007235	+·00001
·001990	·0446	·0148	·007395	·007285	·00729	·00000
·002459	·0496	·0162	·00914	·00899	·00900	+·00001
·002964	·0545	·0169	·01101	·010825	·01083	·00000
·003041	·0551	·0178	·01130	·01110	·01110	·00000
·003679	·0606	·0193	·01367	·01341	·01342	+·00001
·003765	·0614	·0195	·01399	·01372	·01372	·00000
·004438	·0665	·0208	·01649	·01615	·01614	−·00001
·004753	·0690	·0215	·01766	·01728	·01728	·00000
·005945	·0771	·0234	·02209	·02157	·02155	−·00002

TABLE VIII.

Freezing-point data of Scatchard, Jones, and Prentiss [38] on $LiNO_3$:

$$1-g=0{\cdot}374\,C^{1/2}\sigma(C^{1/2})-0{\cdot}260\,C.$$

Molality, m.	$C^{1/2}$.	$1-g_{\text{theor.}}$	$1-\phi_{\text{exp.}}$	$1-g_{\text{exp.}}$	$\theta_{\text{exp.}}-\theta_{\text{theor.}}$
·001	·0316	·0109	·0109	·0109	·0000
·002	·0447	·0151	·0148	·0148	·0000
·005	·0707	·0222	·0218	·0217	+·00001
·010	·1000	·0298	·0293	·0291	+·00004
·020	·1414	·0388	·0368	·0364	+·0001
·050	·2236	·0492	·0480	·0471	+·0006
·100	·3162	·0522	·0552	·0535	−·0008

TABLE IX.

Freezing-point data of Scatchard, Jones, and Prentiss [38] on $NaNO_3$:

$$1-g=0{\cdot}374\,C^{1\,2}\sigma(C^{1/2}).$$

Molality, m.	$C^{1/2}$.	$1-g_{\text{theor.}}$	$1-\phi_{\text{exp.}}$	$1-g_{\text{exp.}}$	$\theta_{\text{exp.}}-\theta_{\text{theor.}}$
·001	·0316	·011	·0109	·0109	·0000
·002	·0447	·016	·0151	·0151	·0000
·005	·0707	·023	·0228	·0227	·0000
·010	·1000	·032	·0311	·0309	+·00006
·020	·1414	·044	·0419	·0415	+·0004
·050	·2236	·062	·0612	·0604	+·0005
·100	·3162	·078	·0803	·0787	−·0001

TABLE X. A.

Freezing-point measurements of Scatchard, Jones, and Prentiss [38] on KNO_3:

$$1-g=0{\cdot}374\,C^{1/2}\sigma(C^{1/2})+0{\cdot}235\,C.$$

Molality, m.	$C^{1/2}$.	$1-g_{\text{theor.}}$	$1-\phi_{\text{exp.}}$	$1-g_{\text{exp.}}$	$\theta_{\text{exp.}}-\theta_{\text{theor.}}$
·001	·0316	·0114	·0114	·0114	·0000
·002	·0447	·0161	·0159	·0159	·0000
·005	·0707	·0247	·0249	·0248	·0000
·010	·1000	·03475	·0348	·0346	+·00001
·020	·1414	·0487	·0485	·0481	+·00007
·050	·2236	·0740	·0748	·0740	·0000
·100	·3162	·1017	·1035	·1019	−·0001

TABLE X. B.

Freezing-point measurements of Adams[1] on KNO_3:

$$1-g=0{\cdot}374\,C^{1/2}\sigma(C^{1/2})+0{\cdot}29\,C.$$

Molality, m.	$C^{1/2}$.	$1-g_{theor.}$	$\theta_{ideal.}$	$\theta_{theor.}$	$\theta_{exp.}$	$\theta_{exp.}-\theta_{theor.}$
·00443	·0665	·0235	·0164	·0160	·0161	+·0001
·00817	·0903	·0315	·03036	·0294	·0295	+·0001
·01565	·125	·043	·05815	·05565	·0558	+·00015
·03874	·1965	·067	·14385	·1342	·1343	+·0001
·05766	·2395	·082	·21404	·1965	·1960	−·0005
·12270	·3495	·118	·4549	·4013	·4017	+·0004

TABLE XI.

Freezing-point measurements of Hovorka and Rodebush[22] on $CsNO_3$:

$$1-g=0{\cdot}374\,C^{1/2}\sigma(C^{1/2}).$$

Molality, m.	$C^{1/2}$.	$1-g_{theor.}$	$\theta_{ideal.}$	$\theta_{theor.}$	$\theta_{exp.}$	$\theta_{exp.}-\theta_{theor.}$
·001	·0316	·0112	·00372	·00368	·00365	−·00003
					·00367	−·00001
·005	·0706	·0239	·01858	·01814	·01807	−·00007
					·01821	+·00007
·010	·1000	·0324	·03716	·03596	·03603	+·00007
					·03596	·00000

TABLE XII.

Freezing-point measurements of Hall and Harkins[19] on $NaIO_3$:

$$1-g=0{\cdot}374\,C^{1/2}\sigma(C^{1/2})+0{\cdot}40\,C.$$

Molality, m.	$C^{1/2}$.	$1-g_{theor.}$	$\theta_{ideal.}$	$\theta_{theor.}$	$\theta_{exp.}$	$\theta_{exp.}-\theta_{theor.}$
·00212	·0460	·017	·00788	·0078	·0077	−·0001
·00499	·0705	·026	·01854	·0180	·0179	−·0001
·00929	·0962	·035	·03452	·0333	·0331	−·0002
·01502	·1227	·045	·05581	·0533	·0530	−·0003
·02868	·169	·061	·10654	·1000	·0997	−·0003
·06329	·2515	·092	·23492	·2133	·2129	−·0004
·1010	·317	·1185	·3746	·3302	·3317	+·0015

TABLE XIII.

Freezing-point data of Hall and Harkins[19] on KIO_3 :

$$1-g=0{\cdot}374\,C^{1/2}\sigma(C^{1/2})+0{\cdot}40\,C.$$

Molality, m.	$C^{1/2}$.	$1-g_{\text{theor.}}$	$\theta_{\text{ideal.}}$	$\theta_{\text{theor.}}$	$\theta_{\text{exp.}}$	$\theta_{\text{exp.}}-\theta_{\text{theor.}}$
·00274	·0523	·019	·01018	·0100	·0099	−·0001
·00506	·0710	·026	·01880	·0183	·01815	−·00015
·00903	·0950	·035	·03356	·0324	·0322	−·0002
·01358	·116	·042	·050455	·0483	·0481	−·0002
·03244	·180	·065	·12047	·1126	·1125	−·0001
·09388	·306	·114	·34826	·3085	·3085	·0000

TABLE XIV.

Freezing-point data of Randall and Scott[35] on Na_2SO_4 :

$$1-g=2\times0{\cdot}374\,I^{1/2}\sigma(I^{1/2})-\frac{4}{3}\times0{\cdot}49\,C.$$

Molality, m.	$I^{1/2}$.	$1-g_{\text{theor.}}$	$\theta_{\text{ideal.}}$	$\theta_{\text{theor.}}$	$\theta_{\text{exp.}}$	$\theta_{\text{exp.}}-\theta_{\text{theor.}}$
·000875	·0513	·035	·00488	·00471	·00480	+·00009
·001797	·0735	·049	·01001	·00952	·00955	+·00003
·003527	·1030	·065	·01966	·01838	·01838	·00000
·005766	·1317	·079	·03213	·02959	·02961	+·00002
·008603	·161	·092	·04794	·04354	·04356	+·00002

TABLE XV. A.

Freezing-point data of Hovorka and Rodebush[22] on K_2SO_4 :

$$1-g=2\times0{\cdot}374\,I^{1/2}\sigma(I^{1/2}).$$

Molality, m.	$I^{1/2}$.	$1-g_{\text{theor.}}$	$\theta_{\text{ideal.}}$	$\theta_{\text{theor.}}$	$\theta_{\text{exp.}}$	$\theta_{\text{exp.}}-\theta_{\text{theor.}}$
·001	·0547	·038	·00557	·00536	·00524	−·00012
					·00522	−·00014
					·00532	−·00004
					·00526	−·00010
					·00531	−·00005
					·00534	−·00002
·005	·122	·077	·02787	·02572	·02573	+·00001
					·02557	−·00015
·010	·173	·102	·05574	·05006	·05004	−·00002
					·05005	−·00001

TABLE XV. B.

Freezing-point data of Hall and Harkins[19] on K_2SO_4:

$$1-g=2\times 0{\cdot}374\,\mathrm{I}^{1/2}\sigma(\mathrm{I}^{1/2}).$$

Molality, m.	$\mathrm{I}^{1/2}$.	$1-g_{\text{theor.}}$	$\theta_{\text{ideal.}}$	$\theta_{\text{theor.}}$	$\theta_{\text{exp.}}$	$\theta_{\text{exp.}}-\theta_{\text{theor.}}$
·00274	·0855	·057	·01527	·0142	·0143	+·0001
·00404	·110	·071	·02252	·0209	·0209	·0000
·00618	·136	·085	·03434	·0314	·0318	+·0004
·01039	·176	·104	·05791	·0519	·0521	+·0002
·01756	·229	·126	·09788	·0856	·0855	−·0001
·02608	·280	·145	·1452	·1241	·1241	·0000

TABLE XVI. A.

Freezing-point data of Randall and Scott[35] on $Ba(NO_3)_2$:

$$1-g=2\times 0{\cdot}374\,\mathrm{I}^{1/2}\sigma(\mathrm{I}^{1/2})+\frac{4}{3}\times 0{\cdot}41\ \mathrm{C}.$$

Molality, m.	$\mathrm{I}^{1/2}$.	$1-g_{\text{theor.}}$	$\theta_{\text{ideal.}}$	$\theta_{\text{theor.}}$	$\theta_{\text{exp.}}$	$\theta_{\text{exp.}}-\theta_{\text{theor.}}$
·001669	·071	·049	·00930	·00884	·00879	−·00005
·005220	·125	·082	·02909	·02671	·02667	−·00004
·007381	·149	·095	·04113	·03723	·03715	−·00008
·008667	·161	·102	·04829	·04336	·04336	·00000
·011667	·187	·1155	·06500	·05748	·05743	−·00005
·018114	·234	·138	·10089	·0870	·0869	−·0001
·026490	·282	·1605	·14750	·1238	·1239	+·0001
·038505	·340	·185	·2143	·1746	·1749	+·0003

TABLE XVI. B.

Freezing-point data of Hovorka and Rodebush[22] on $Ba(NO_3)_2$:

$$1-g=2\times 0{\cdot}374\, I^{1/2}\sigma(I^{1/2})+\frac{4}{3}\times 0{\cdot}41\, C.$$

Molality, m.	$I^{1/2}$.	$1-g_{\text{theor.}}$	$\theta_{\text{ideal.}}$	$\theta_{\text{theor.}}$	$\theta_{\text{exp.}}$	$\theta_{\text{exp.}}-\theta_{\text{theor.}}$
·001	·0547	·0385	·00557	·00536	·00539	+·00003
					·00538	+·00002
·005	·122	·080	·02787	·02564	·02575	+·00011
					·02565	+·00001
·010	·173	·1075	·05574	·04974	·04980	+·00006
					·04988	+·00014

TABLE XVII. A.

Freezing-point data of Hovorka and Rodebush[22] on $MgSO_4$:

$$1-g=4\times 0{\cdot}374\, I^{1/2}\sigma(I^{1/2}).$$

Molality, m.	$I^{1/2}$.	$1-g_{\text{theor.}}$	$\theta_{\text{ideal.}}$	$\theta_{\text{theor.}}$	$\theta_{\text{exp.}}$	$\theta_{\text{exp.}}-\theta_{\text{theor.}}$
·001	·0632	·0864	·00372	·00340	·00339	−·00001
					·00336	−·00004
·005	·1412	·174	·01858	·01535	·01519	−·00016
					·01525	−·00010
·010	·2000	·228	·03716	·02869	·02882	+·00013
					·02868	−·00001

TABLE XVII. B.

Freezing-point data of Hall and Harkins[19] on $MgSO_4$:

$$1-g=4\times 0{\cdot}374\, I^{1/2}\sigma(I^{1/2}).$$

Molality, m.	$I^{1/2}$.	$1-g_{\text{theor.}}$	$\theta_{\text{ideal.}}$	$\theta_{\text{theor.}}$	$\theta_{\text{exp.}}$	$\theta_{\text{exp.}}-\theta_{\text{theor.}}$
·003201	·1132	·144	·01190	·0102	·0100	−·0002
·00535	·1464	·180	·01988	·0163	·0160	−·0003
·00746	·1726	·205	·02772	·0219	·0217	−·0002
·01310	·2290	·252	·04868	·0364	·0362	−·0002
·02668	·326	·319	·09911	·0675	·0673	−·0002

TABLE XVIII.

Freezing-point data of Hovorka and Rodebush[22] on $CuSO_4$:

$$1-g=4\times 0{\cdot}374\,\Gamma^{1/2}\sigma(\Gamma^{1/2})+1{\cdot}7\ \text{C.}$$

Molality, m.	$\Gamma^{1/2}$.	$1-g_{\text{theor.}}$	$\theta_{\text{ideal.}}$	$\theta_{\text{theor.}}$	$\theta_{\text{exp.}}$	$\theta_{\text{exp.}}-\theta_{\text{theor.}}$
·001	·0632	·088	·00372	·00340	·00331	−·00009
					·00343	+·00004
·005	·1412	·1825	·01858	·01519	·01525	+·00006
					·01515	−·00004
·010	·2000	·245	·03716	·02806	·02810	+·00004
					·02799	−·00007

TABLE XIX.

Freezing-point data of Hall and Harkins[19] on $La(NO_3)_3$:

$$1-g=0{\cdot}374\,\Gamma^{1/2}\sigma(\Gamma^{1/2})-\frac{3}{2}\times 2{\cdot}6\ \text{C.}$$

Molality, m.	$\Gamma^{1/2}$.	$1-g_{\text{theor.}}$	$\theta_{\text{ideal.}}$	$\theta_{\text{theor.}}$	$\theta_{\text{exp.}}$	$\theta_{\text{exp.}}-\theta_{\text{theor.}}$
·00132	·089	·083	·00981	·0090	·0091	+·0001
·00354	·146	·121	·02631	·0231	·0234	+·0003
·00806	·220	·153	·05990	·0507	·0509	+·0002
·00857	·227	·155	·06362	·05375	·0537	−·00005

TABLE XX.

Freezing-point data of Hovorka and Rodebush[22] on $La_2(SO_4)_3$:

$$1-g=6\times 0{\cdot}374\,\Gamma^{1/2}\sigma(\Gamma^{1/2}).$$

Molality, m.	$\Gamma^{1/2}$.	$1-g_{\text{theor.}}$	$\theta_{\text{ideal.}}$	$\theta_{\text{theor.}}$	$\theta_{\text{exp.}}$	$\theta_{\text{exp.}}-\theta_{\text{theor.}}$
·001	·1224	·234	·00929	·00712	·00719	+·00007
					·00709	−·00003
·0035	·229	·378	·032515	·02022	·02022	·00000
					·02010	−·00012
·005	·274	·428	·04645	·02656	·02590	−·00066
					·02600	−·00056
·00819	·350	·500	·076085	·03804	·03801	−·00003
					·03824	+·00016

These tables call for a few comments. It will be noticed that with suitably chosen values of the interaction coefficients λ there is agreement between the observed and calculated values of θ, usually to within one or two ten-thousandths of a degree ; sometimes the agreement is rather less good, and in other cases it is nearly ten times better. The degree of agreement depends at least partly on the experimental accuracy. Thus the comparatively recent measurements of Randall and Vanselow[36] and of Hovorka and Rodebush[22] give a more exact agreement than the older measurements of Adams[1] and of Hall and Harkins[19]. On the other hand the still more recent measurements of Scatchard, Jones, and Prentiss[38],[39] give rather greater fluctuations. No measurements earlier than those of Adams are sufficiently accurate to be worth including. The measurements of Karagunis, Hawkinson, and Damköhler[24] have also been rejected on the grounds of inaccuracy, at least at high dilutions. When the available data for KCl at high dilutions are plotted on a large scale, those of Adams[1], of Hovorka and Rodebush[22], and of Scatchard and Prentiss[39] are in quite fair agreement with one another, but those of Karagunis, Hawkinson, and Damköhler[24] deviate from the others by as much as ·003° C., which is five times as great as the *maximum* divergence between the other three sets of data. It therefore seems most probable that the data of Karagunis, Hawkinson, and Damköhler are unreliable at these high dilutions ; whether their data at higher concentrations are more trustworthy is a question on which we express no opinion. Another set of freezing-point measurements not included are those of Scatchard and Prentiss[39] on the halides of ammonium. These measurements show large disagreement with the limiting law of Debye and Hückel, and so cannot be fitted either by formulæ of the Debye-Hückel type or by our formulæ. No explanation of this peculiarity of the ammonium salts has yet been offered. In those cases where more than one set of measurements has been made on the same electrolyte each set has been tabulated separately. When the two sets of data agree fairly well, λ value has been chosen either to give the best agreement with the whole available material or, if one set of data appears to be of higher accuracy than the remainder, to give the best agreement with this set. The data of Adams

and those of Scatchard and Prentiss on KCl are each fitted accurately by our formulæ, but only with different values for the interaction coefficient $\lambda_{K,Cl}$. It is difficult to decide which set of data is the more reliable. That of Adams is considerably earlier, and made with less elaborate apparatus, but gives $g\lambda_{K,Cl}$ value at 0° C. considerably closer to the value at 20° C. obtained from the electrometric and solubility measurements of Güntelberg[18] (see below). There is a similar discrepancy between the data of Adams on KNO_3 and those of Scatchard, Jones, and Prentiss. We lay particular stress on the remarkably good agreement between our formulæ and the data at high dilutions of Randall and Vanselow on HCl and TlCl. This affords the strongest possible confirmation of the limiting law of Debye and Hückel. The apparent disagreement between experiment and theory reported by Randall and Vanselow is entirely due to their use of an extrapolation which itself contradicts the theory.

The only electrometric measurements in dilute solutions of a sufficiently high accuracy for comparison with our formulæ are those for the cell

$$\text{Ag} \mid \text{AgCl} \mid \text{solution of HCl} \mid \text{H}_2, \text{Pt}.$$

Leaving aside older and less accurate measurements, those of Güntelberg[18] at 20° C., and those of Randall and Young[37] and of Carmody[8] at 25° C. are all in excellent agreement with those of Harned and Ehlers[21], which cover the temperature range 0° C. to 35° C. In Table XXI. are given the values of the rational activity coefficient $f_{H,Cl}$ at various molalities and temperatures computed from Harned and Ehlers's data by means of formula (14). The values in millivolts of E° given at the top of the table are given by Harned and Ehlers's formula

$$E^0 = -222{\cdot}39 + 0{\cdot}6455\,(t-25) - 3{\cdot}28\times10^{-3}(t-25)^2 - 9{\cdot}9\times10^{-6}(t-25)^3,$$

where t denotes temperature on the Celsius scale. The data of Güntelberg are also included. At each molality the variation of $f_{H,Cl}$ with the temperature is very slight, and probably no greater than the experimental error. In the last column are given values of $f_{H,Cl}$ calculated by using formula (66) with the value 0·240 for $\lambda_{H,Cl}$, the same

Table XXI.

Values of $f_{H,\,Cl}$ from electromotive-force measurements of Harned and Ehlers[21].

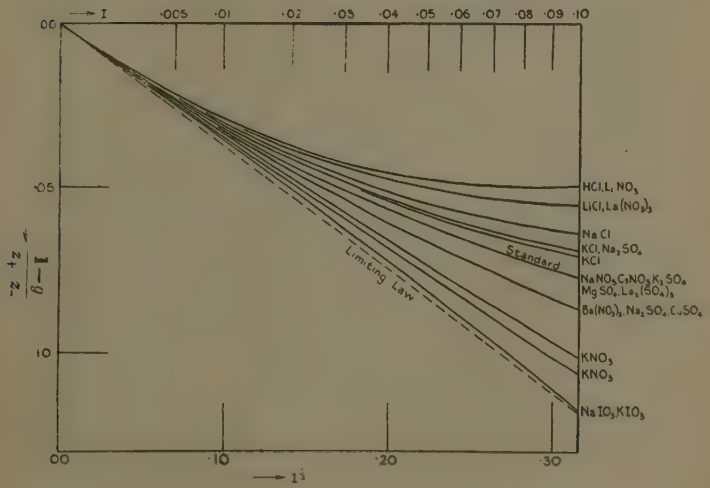
Temperature in °C.	0.	5.	10.	15.	20.	20. (Güntelberg).	25.	30.	35.	Calculated for 20° C.
$\log_e 10 \cdot \frac{RT}{F}$ in m.v..	54·19	55·18	56·18	57·17	58·16	58·16	59·15	60·14	61·13	..
E^0 in m.v.	−236·32	−233·91	−231·30	−228·51	−225·54	−225·50	−222·39*	−219·08	−215·61	..
Molality.										
·005	·930	·929	·930	·930	·929	..	·928	·926	·925	·929
·006	·924	·924	·924	·924	·924	..	·923	·920	·919	·923
·007	·918	·918	·918	·919	·918	..	·917	·915	·913	·918
·008	·914	·913	·914	·915	·914	..	·913	·911	·910	·914
·009	·909	·909	·910	·910	·910	..	·908	·906	·905	·910
·010	·905	·905	·906	·906	·906	·908	·905	·902	·901	·906
·020	·879	·880	·879	·880	·880	·880	·878	·875	·875	·877
·030	·859	·859	·858	·860	·859	..	·857	·854	·854	·858
·040	·846	·846	·845	·846	·845	..	·842	·839	·839	·844
·050	·836	·836	·834	·835	·834	·836	·831	·828	·827	·833
·060	·828	·828	·826	·827	·826	..	·823	·821	·818	·824
·070	·820	·820	·819	·819	·818	..	·815	·811	·810	·817
·080	·815	·814	·813	·812	·812	..	·809	·797	·804	·811
·090	·810	·809	·808	·808	·808	..	·804	·799	·799	·806
·100	·805	·804	·803	·802	·801	·802	·799	·794	·797	·801

* Carmody's measurements are best fitted by $E^0 = -222{\cdot}2$.
Randall and Young's measurements are best fitted by $E^0 = -222{\cdot}1$.

as the value used at 0° C. to fit the freezing-point data of Randall and Vanselow.

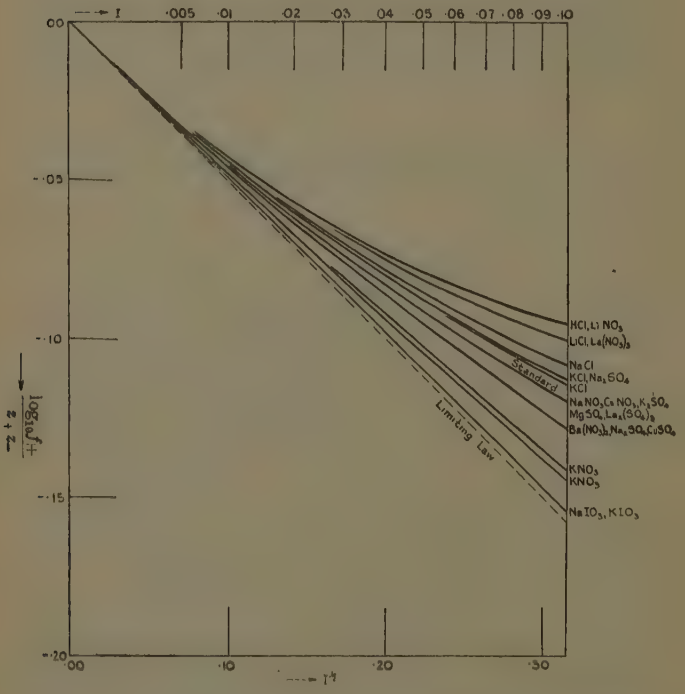
In figs. 1 and 2 are plotted the curves for $1-g/z_+ \mid z_- \mid$ and for $\log_{10} f_\pm/z_+ \mid z_- \mid$ respectively. It is to be noticed that our formulæ are applicable not only to such electrolytes as are covered by the original Debye–Hückel theory, but also those, such as the nitrates and iodates, with mean ionic diameters too small for the assumptions of Debye and Hückel to be valid, and which require special treatment such as those of Bjerrum[4], of Müller[31], and of Gronwall[11]. It is also remarkable that our formulæ apply to electrolytes of all valence types, including even $La_2(SO_4)_3$, for which at the highest concentration considered g has the value 0·50. If we take two ten-thousandths of a degree as an average value of the degree of agreement between the formulæ and the experimental data, this corresponds to an accuracy of about 0·06 per cent. in g for a decimolal solution of a binary electrolyte. For a uni-univalent electrolyte this means an accuracy of about 0·8 per cent. in $1-g$, of 2 per cent. in $\log f$, of 0·8 per cent. in $\log_{10} f$, and so of 0·2 per cent. in f. An accuracy of 0·2 per cent. in the value of f is adequate

Fig. 1.



for all practical purposes. In fact we might consider ourselves extremely fortunate if values of activity coefficients were known with an accuracy approaching this. For electrolytes of varying valence type the accuracy will be roughly comparable at the same ionic strength.

Fig. 2.



It is quite possible, if not probable, that some electrolytes of the higher valence types are not completely dissociated at ionic strengths as high as 0·1. Still, our formulæ appear to be applicable, and this is to be expected as long as the electrolyte is mostly dissociated, for the incomplete dissociation will then contribute a term linear in the concentration, and this effect will be included in the specific interaction coefficient $\lambda_{R,X}$.

We do not claim that the values assigned to the interaction coefficients $\lambda_{R,X}$ are absolutely the most probable. Strictly the method of least squares ought to be applied, but the values assigned will be sufficiently accurate for most purposes. In some cases it is obvious from the values of $\theta_{exp.}-\theta_{theor.}$ that the agreement could, by a slight adjustment in the value of $\lambda_{R,X}$, be improved, but not sufficiently to make a recomputation worth while. The λ values given will in any case require revision as better experimental data accumulate. At the present moment the λ values used will certainly give values for activity coefficients as reliable as the best available experimental data. As it is over ten years since Lewis and Randall[27] published their provisional values for activity coefficients it is time that these were revised.

There is one further point worthy of notice, that is, the number of electrolytes of various valence type for which the interaction coefficient λ is approximately zero This means simply that in selecting our definition of the standard electrolytes we have made a good choice. The data for actual electrolytes lie scattered on both sides of the standard electrolyte, and often near to it. If, as often happens, a value is required for the activity coefficient of some electrolyte, and there are no experimental data available, we strongly recommend as a reasonable approximation the values given by the formula

$$\log_{10} f_{\pm} = \log_{10} f_{\pm}^{stand.} = -0{\cdot}50^{\,z_+ \mid z_- \mid} \frac{I^{1/2}}{1+I^{1/2}}, \quad . \quad . \quad . \quad (71)$$

and obtainable from Table I. The alternative use of the limiting law formula of Debye and Hückel,

$$\log_{10} f_{\pm} = -0{\cdot}50\, z_+ z_- I^{1/2}, \quad . \quad . \quad . \quad . \quad . \quad (72)$$

is to be deprecated, as it will usually be seriously inaccurate at ionic strengths much exceeding 0·01.

7. *Application to Mixed Electrolytes of same Valence Type.*

The important advantage of our theory over that of Debye and Hückel is its applicability to mixtures of two or more electrolytes. We shall commence with a discussion of solutions containing electrolytes of only one valence type. Let us consider a set of solutions containing two electrolytes (R, X), and (R′, X′) of the same valence

type (z_+, z_-), and all of the same total electrolyte concentration C expressed in moles/litre. Let $f^{\mathrm{R},\mathrm{X}}_{\mathrm{R},\mathrm{X}}$ denote the mean activity coefficient of (R, X) in the solution containing only (R, X); a similar definition holds for $f^{\mathrm{R}',\mathrm{X}}_{\mathrm{R}',\mathrm{X}}$. Let $f^{\mathrm{R},\mathrm{X}}_{\mathrm{R}'',\mathrm{X}''}$ denote the mean activity coefficient of another electrolyte (R'', X''), also of the same valence type, present in very small amount in a solution containing effectively only (R, X); a similar definition holds for $f^{\mathrm{R}'',\mathrm{X}'}_{\mathrm{R}'',\mathrm{X}''}$. As a special case $f^{\mathrm{R},\mathrm{X}}_{\mathrm{R}',\mathrm{X}'}$ will denote the mean activity coefficient of (R', X') in a solution containing effectively only (R, X). Then, according to (57), we have

$$\log_{10} f^{\mathrm{R},\mathrm{X}}_{\mathrm{R}'',\mathrm{X}''} = -0{\cdot}50\frac{z_+ \mid z_- \mid \mathrm{I}^{1/2}}{1+\mathrm{I}^{1/2}} + \mathrm{C}\frac{q}{2}\{\lambda_{\mathrm{R}'',\mathrm{X}}+\lambda_{\mathrm{R},\mathrm{X}''}\}, \quad . \quad . \quad . \quad (73)$$

and similarly

$$\log_{10} f^{\mathrm{R}',\mathrm{X}'}_{\mathrm{R}'',\mathrm{X}''} = -0{\cdot}50\frac{z_+ \mid z_- \mid \mathrm{I}^{1/2}}{1+\mathrm{I}^{1/2}} + \mathrm{C}\frac{q}{2}\{\lambda_{\mathrm{R}'',\mathrm{X}'}+\lambda_{\mathrm{R}',\mathrm{X}''}\} \; . \quad . \quad . \quad (74)$$

For the mean activity coefficient $f^{(x)}_{\mathrm{R}'',\mathrm{X}''}$ in the solution containing the electrolytes (R, X) and (R', X') in the ratio $1-x$ to x, we have, according to (57),

$$\log_{10} f^{(x)}_{\mathrm{R}'',\mathrm{X}''} = -\frac{0{\cdot}50\, z_+ \mid z_- \mid \mathrm{I}^{1/2}}{1+\mathrm{I}^{1/2}} + \mathrm{C}\frac{q}{2}\{\lambda_{\mathrm{R}'',\mathrm{X}}(1-x)+\lambda_{\mathrm{R}'',\mathrm{X}'}x + \lambda_{\mathrm{R},\mathrm{X}''}(1-x)+\lambda_{\mathrm{R}',\mathrm{X}''}x\} \; . \quad . \quad . \quad . \quad . \quad (75)$$

By comparison of (75) with (73) and (74) we obtain

$$\log_{10} f^{(x)}_{\mathrm{R}'',\mathrm{X}''} = \log_{10} f^{\mathrm{R},\mathrm{X}}_{\mathrm{R}'',\mathrm{X}''} + x\{\log_{10} f^{\mathrm{R},\mathrm{X}'}_{\mathrm{R}'',\mathrm{X}''} - \log_{10} f^{\mathrm{R},\mathrm{X}}_{\mathrm{R}'',\mathrm{X}''}\}, \quad (76)$$

so that $\log f_{\mathrm{R}'',\mathrm{X}''}$ is a linear function of x. This is the essential content of Brönsted's [7] principle of linear variation, which dates back to 1923, and is older than the theory of Debye and Hückel.

From the symmetry of (73) we see that

$$\log_{10} f^{\mathrm{R},\mathrm{X}}_{\mathrm{R}',\mathrm{X}'} = \log_{10} f^{\mathrm{R}',\mathrm{X}'}_{\mathrm{R},\mathrm{X}} \; . \quad . \quad . \quad . \quad . \quad (77)$$

If this result is true it is of extreme practical importance. For it enables us, for instance, to deduce the mean activity

coefficient $f^{H,\,Cl}_{K,\,ClO_4}$ of $KClO_4$ present in small quantity in a large excess of HCl from the value of $f^{K,\,ClO_4}_{H,\,Cl}$ the mean activity coefficient of HCl present in small quantity in a large excess of $KClO_4$. The quantity $f^{K,\,ClO_4}_{H,\,Cl}$ can be directly measured electrometrically by means of hydrogen and silver—silver chloride electrodes, whereas a direct measurement of $f^{H,\,Cl}_{K,\,ClO_4}$ is impracticable owing to lack of electrodes reversible to K^+ and ClO_4^- in dilute solution.

If the two electrolytes (R, X) and (R′, X′) have an ion in common, say the anion X, then (75) becomes

$$\left.\begin{aligned}\log_{10} f^{(x)}_{R'',\,X''} &= -0{\cdot}50\frac{z_+ \mid z_- \mid I^{1/2}}{1+I^{1/2}} + C\frac{q}{2}\{\lambda_{R'',\,X} \\ &\quad + \lambda_{R,\,X''}(1-x) + \lambda_{R',\,X''}x, \\ &= \log_{10} f^{R,\,X}_{R'',\,X''} + xC\frac{q}{2}\{\lambda_{R',\,X''} - \lambda_{R,\,X''}\}.\end{aligned}\right\} \quad . \quad (78)$$

We see that not only is $f_{R'',\,X''}$ a linear function of x, but the coefficient of x is independent of the nature of the common anion of the two electrolytes present in large amount and of the cation of the third electrolyte present in very small amount. By applying (78) to the solutions containing respectively only (R, X) (i. e., $x=0$) and only (R′, X′) (i. e., $x=1$), we obtain

$$\log_{10} f^{R',\,X'}_{R'',\,X''} - \log_{10} f^{R,\,X}_{R'',\,X''} = C\frac{q}{2}\{\lambda_{R',\,X''} - \lambda_{R,\,X''}\}, \quad . \quad (79)$$

and so the ratio of the value $f^{R',\,X'}_{R'',\,X''}$ of mean activity coefficient of (R″, X″) in the solution of (R′, X′) to its value $f^{(R,\,X)}_{R'',\,X''}$ in the solution of (R, X) is independent of the nature of the cation R″ and of the anion X. This statement contains one of the most important predictions of Brönsted's[5] theory of the specific interaction of ions. The truth of this statement has been verified in numerous cases by Brönsted[5].

For the osmotic coefficient $g^{(x)}$ of a solution containing (R, X) and (R′, X′) in the ratio $1-x$ to x we have, according to (62),

$$1-g^{(x)} = 0{\cdot}374\, z_+ \mid z_- \mid I^{1/2}\sigma(I^{1/2}) - 2{\cdot}30\, C\frac{q}{2}\{\lambda_{R,\,X}(1-x)^2 + (\lambda_{R',\,X} + \lambda_{R,\,X'})x(1-x) + \lambda_{R',\,X'}x^2\}, \quad . \quad (80)$$

so that the osmotic coefficient $g^{(x)}$ is a quadratic function of x. This was first pointed out by Güntelberg[18], and is contrary to Brönsted's[5] original formulation of the theory of linear variation. In the special case that the electrolytes have a common ion, say the anion, (80) simplifies to

$$1-g=0{\cdot}374\,z_+|\,z_-\,|\Gamma^{1/2}\sigma(\Gamma^{1/2})-2{\cdot}30\,\mathrm{C}\frac{q}{2}\{\lambda_{\mathrm{R,X}}(1-x)+\lambda_{\mathrm{R',X}}x\}, \quad . \quad . \quad . \quad (81)$$

and in this case the osmotic coefficient is a linear function of x. If we denote by $g^{\mathrm{R,X}}$ and $g^{\mathrm{R',X}}$ the values of g in solutions containing respectively only (R, X) and only (R′, X′), we may write (81) in the form

$$\left.\begin{aligned}1-g^{(x)}&=1-g^{\mathrm{R,X}}-x\,2{\cdot}30\,\mathrm{C}\frac{q}{2}\{\lambda_{\mathrm{R',X}}-\lambda_{\mathrm{R,X}}\},\\&=1-g^{\mathrm{R,X}}-x(g^{\mathrm{R',X}}-g^{\mathrm{R,X}}),\end{aligned}\right\} \quad . \quad (82)$$

and in this case the osmotic coefficient $g^{(x)}$ is a linear function of x. If we apply (78) to the case that the anion X″ is identical with X (as well as X′), we obtain

$$\log_{10}f^{(x)}_{\mathrm{R'',X}}=\log_{10}f^{\mathrm{R,X}}_{\mathrm{R'',X}}+x\,\mathrm{C}\,\frac{q}{2}\{\lambda_{\mathrm{R',X}}-\lambda_{\mathrm{R,X}}\}. \quad . \quad (83)$$

In particular we have

$$\log_{10}f^{(x)}_{\mathrm{R,X}}=\log_{10}f^{\mathrm{R,X}}_{\mathrm{R,X}}+x\mathrm{C}\frac{q}{2}\{\lambda_{\mathrm{R',X}}-\lambda_{\mathrm{R,X}}\} \quad . \quad (84)$$

and

$$\log_{10}f^{(x)}_{\mathrm{R',X}}=\log_{10}f^{\mathrm{R,X}}_{\mathrm{R',X}}+x\mathrm{C}\frac{q}{2}\{\lambda_{\mathrm{R',X}}-\lambda_{\mathrm{R,X}}\}. \quad . \quad (85)$$

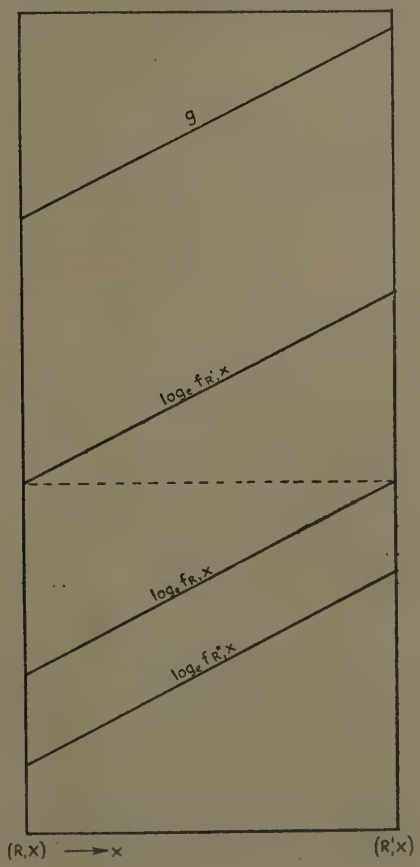
The relations (82), (83), (84), (85) are represented diagrammatically in fig. 3, due to Brönsted[7]. When $\log_e f^{(x)}_{\mathrm{R'',X}}$ is plotted against x a straight line is obtained with a slope independent of the nature of R″, and the same as the slope of the plot of $g^{(x)}$. It is also to be noticed that the value of $f_{\mathrm{R,X}}$ at $x=1$ is the same as that of $f_{\mathrm{R',X}}$ at $x=0$, in accordance with the relation (77).

The strongest experimental support for the formulæ of this section is due to Güntelberg[18]. He measured the electromotive force of the cells

$$\mathrm{Ag}\,\Big|\,\mathrm{AgCl}\,\Big|\,\begin{matrix}0{\cdot}1x\,\mathrm{M\ AlkCl}\\0{\cdot}1(1-x)\,\mathrm{M\ HCl}\end{matrix}\,\Big|\,\mathrm{H_2,\ Pt\ at\ 20^\circ\ C.},$$

where Alk denotes one of the alkali metals Li, Na, K, Cs, and so obtained values for $\log f^{(x)}_{H,\,Cl} - \log f^{H,\,Cl}_{H,\,Cl}$. When this quantity is plotted against the fractional quantity x

Fig. 3.



of the alkali chloride, the linearity of $\log f^{(x)}_{H,\,Cl}$ is established within the exceptionally high degree of accuracy of 0·02 millivolts ; this corresponds to an accuracy of 0·04 per cent. in $f_{H,\,Cl}$. From these measurements we can calculate

values for $\lambda_{\mathrm{Alk,\,Cl}}-\lambda_{\mathrm{H,\,Cl}}$. Hence, if we know the solubility of some slightly soluble chloride RCl in decimolal HCl we can compute its solubility in decimolal AlkCl. For its mean solubility $S_{\mathrm{R,\,Cl}}$ is inversely proportional to its activity coefficient, and so, according to (83), is given by

$$\left.\begin{aligned}\log_{10}S^{\mathrm{Alk,\,Cl}}_{\mathrm{R,\,Cl}}-\log_{10}S^{\mathrm{H,\,Cl}}_{\mathrm{R,\,Cl}}&=-\log_{10}\gamma^{\mathrm{Alk,\,Cl}}_{\mathrm{R,\,Cl}}+\log_{10}\gamma^{\mathrm{H,\,Cl}}_{\mathrm{R,\,Cl}}\\&=-C\tfrac{1}{2}(\lambda_{\mathrm{Alk,\,Cl}}-\lambda_{\mathrm{H,\,Cl}})\\&=-\log_{10}\gamma^{\mathrm{Alk,\,Cl}}_{\mathrm{H,\,Cl}}+\log_{10}\gamma^{\mathrm{H,\,Cl}}_{\mathrm{H,\,Cl}}\end{aligned}\right\}. \quad (86)$$

Güntelberg[18] tested this relation using the slightly soluble salt $[Co(NO_2)(SCN)(NH_3)_4]Cl$. The results are given in Table XXII. The first column gives the composition of the solution, the second the value of $\lambda_{\mathrm{Alk,\,Cl}}$

TABLE XXII.

Interaction coefficients $\lambda_{\mathrm{Alk,\,Cl}}-\lambda_{\mathrm{H,\,Cl}}$ from various measurements.

Solution.	E.M.F. at 20° C. Güntelberg[18].	Solubility at 20° C. Güntelberg[18].	Freezing-point at 0° C. Scatchard[39].	Freezing-point at 0° C. Adams[1].
0·1 M LiCl	−0·014	−0·012	−0·045	....
0·1 M NaCl	−0·084	−0·078	−0·123	....
0·1 M KCl	−0·168	−0·168	−0·184	−0·168
0·1 M CsCl	−0·292	−0·294	....	....

$-\lambda_{\mathrm{H,Cl}}$ obtained from the electrometric measurements, and the third the value of the same quantity obtained from the solubility measurements. The agreement between the values in these two columns is remarkably good. In the fourth column are given the values of $\lambda_{\mathrm{Alk,Cl}}-\lambda_{\mathrm{H,Cl}}$ calculated from the values of λ given in Table II. The discrepancy between the values in the second and third columns on the one hand and those in the fourth column on the other may be due to the fact that the former are values at 20° C., whereas the latter are values at 0° C. There is no theoretical reason why the λ values should be independent of the temperaure, though, admittedly, the differences are greater than we should expect. As the mean activity coefficient $f^{\mathrm{H,Cl}}_{\mathrm{H,Cl}}$

of HCl in decimolal solution has almost exactly the same value at 20° C. as at 0° C., it is rather surprising that there should be such a large dependence on the temperature in the case of the alkali chlorides. An alternative explanation is that the freezing-point measurements of Scatchard and Prentiss are in error. Those of Adams for KCl yield a value for $\lambda_{K,Cl}-\lambda_{H,Cl}$ at 0° C. in exact agreement with the value obtained at 20° C. from Güntelberg's measurements. The values of $\lambda_{H,Cl}$ can hardly be at fault, as the electrometric data of so many workers[18], [37], [8], [21] are in good agreement.

The predictions of the theory of specific interaction of ions are further supported by considerable quantity of solubility data obtained by Brönsted. For details we refer the reader to the original paper[5]. Generally speaking, the more accurate the experiments the more exact is the agreement with the theory.

8. *Applications to Mixed Electrolytes of Different Valence Type.*

In its application to solutions containing electrolytes of only one valence type the predictions of the present theory are the same as those of the original version due to Brönsted[5]. It is in the application to electrolytes of varying valence type that the present treatment gives new results. Let us, for example, consider the ratio r of the mean solubility of various types of slightly soluble electrolytes in 0·1 molal KNO_3 to their solubility in 0·1 molal $NaNO_3$. In the case of a uni-univalent electrolyte R′X we have

$$\left.\begin{aligned}\log_{10} r_{R'X} &= \log_{10} S_{R'X}^{KNO_3} - \log_{10} S_{R'X}^{NaNO_3} \\ &= -\log_{10}\gamma_{R'X}^{KNO_3} + \log_{10}\gamma_{R'X}^{NaNO_3} \\ &= \tfrac{1}{2}C(\lambda_{Na,X}-\lambda_{K,X}),\end{aligned}\right\} \quad . \quad (87)$$

where C in this case is 0·1. Similarly for an electrolyte $R''X_2$ with a bivalent cation R″ and the same anion X we have

$$\left.\begin{aligned}\log_{10} r_{R''X_2} &= \log_{10} S_{R''X_2}^{KNO_3} - \log_{10} S_{R''X_2}^{NaNO_3} \\ &= -\log_{10}\gamma_{R''X_2}^{KNO_3} + \gamma_{R''X_2}^{NaNO_3} \\ &= \frac{1}{2}\cdot\frac{4}{3}C\ \{\lambda_{Na,X}-\lambda_{K,X}\}.\end{aligned}\right\} \quad . \quad (88)$$

Finally, for an electrolyte $R'''X_3$ with the same anion, but a trivalent cation R''', we have

$$\left.\begin{aligned}\log_{10}\gamma_{R'''X_3} = &\log S^{KNO_3}_{R'''X_3} - \log_{10} S^{NaNO_3}_{R'''X_3} \\ &-\log_{10}\gamma^{KNO_3}_{R'''X_3} + \log_{10}\gamma^{NaNO_3}_{R'''X_3} \\ &\frac{1}{2}\cdot\frac{3}{2}C\{\lambda_{Na,X} - \lambda_{K,X}\}.\end{aligned}\right\} \quad . \quad . \quad . \quad (89)$$

From (87), (88), (89) we deduce that the ratio r is determined completely by the valency, but is otherwise

TABLE XXIII.

Ratio of solubility in 0·1 M KNO_3 to that in 0·1 M $NaNO_3$ of various Tetranitro-diammine-cobaltiates from data of Brönsted[5] at 20° C.

	$r \quad S^{KNO_3}/S^{NaNO_3}$.
Univalent cations	1·0315 calculated.
$[Co(NH_3)_4C_2O_4]^-$	1·034
$[Co(NH_3)_4CO_3]^+$	1·032
Ag^+	1·034
$N(CH_3)_4^+$	1·034
Bivalent cations	1·0422 calculated.
$[Co(NH_3)_5Cl]^+$	1·041
$[Co(NH_3)_5NO_3]^{++}$	1·041
Trivalent cations	1·0476 calculated.
$[Co(NH_2.C_2H_4.NH_2)_3]^{+++}$	1·045
$[Co(NH_3)_5H_2O]^{+++}$	1·047

independent of the specific nature of the cation R', R'', or R'''. This result was predicted by Brönsted. But from formulæ (87), (88), (89) we can go further, and deduce a definite relation between the ratios r for the three types of solute, namely,

$$(\gamma_{R'X})^{2/1} = (\gamma_{R''X_2})^{3/2} = (\gamma_{R'''X_3})^{4/3}. \quad . \quad . \quad . \quad (90)$$

To test this relation we may take Brönsted's[5] data for the solubilities of various salts with the anion $[Co(NO_2)_4(NH_3)_2]^-$. The data are given in Table XXIII.

together with a set of values for the three ratios $r_{R^{n+}X^-}$, $r_{R^{n+}X_2^-}$ and $r_{R^{n+}X_3^-}$ which satisfy the relation (90). There is agreement to within 2 parts in 1000. More perfect agreement is hardly to be expected when it is remembered that, owing to the presence of the solute salts, the total ion concentration varies from case to case between 0·100 and 0·105, and it is, therefore, an approximation to regard the solutions as merely 0·1 M KNO_3 and 0·1 M $NaNO_3$.

Another test of the present theory, involving electrolytes of more than one valence type, is provided by the electrometric measurements of Randall and Breckenbridge[34]. These authors used cells of the type

$$\mathrm{Ag} \mid \mathrm{AgCl} \mid \text{Solution of } \mathrm{HCl} \mid \mathrm{BaCl_2} \mid \mathrm{H_2}, \mathrm{Pt}$$

and

$$\mathrm{Ag} \mid \mathrm{AgCl} \mid \text{Solution of } \mathrm{HCl} \mid \mathrm{LaCl_3} \mid \mathrm{H_2}, \mathrm{Pt}.$$

From the measured electromotive force we can calculate the activity coefficient of HCl in each solution. The authors found that the activity coefficient was not determined completely by the total ionic strength nor by the total equivalent concentration. But this is what we should expect, for according to (52) it should be given, for the solutions containing $BaCl_2$, by

$$\left.\begin{aligned}\log_{10} f_{\mathrm{H,Cl}} = -0{\cdot}50\,\frac{I^{1/2}}{1+I^{1/2}} &+ \tfrac{1}{2}\lambda_{\mathrm{H,Cl}}c_{\mathrm{Cl^-}} \\ &+ \tfrac{1}{2}\lambda_{\mathrm{H,Cl^-Cl^-}}c_{\mathrm{Cl^-}}c_{\mathrm{Cl^-}} + \tfrac{1}{2}\lambda_{\mathrm{Ba,Cl^-Cl^-}}c_{\mathrm{Cl^-}}c_{\mathrm{Cl^-}} \\ -0{\cdot}50\,\frac{I^{1/2}}{1+I^{1/2}} &+ \lambda_{\mathrm{H,Cl}}c_{\mathrm{Cl^-}} \\ &+ (\tfrac{1}{2}\lambda_{\mathrm{Ba,Cl}} - \tfrac{1}{2}\lambda_{\mathrm{H,Cl}})(c_{\mathrm{Cl^-}} - c_{\mathrm{H^+}}).\end{aligned}\right\} \quad . \quad . \quad . \quad (91)$$

The value of λ_{HCl} is 0·25. If we assign the value 0·22 to $\lambda_{\mathrm{Ba,Cl}}$, then (91) becomes

$$\log_{10} f_{\mathrm{H,Cl}} = -0{\cdot}50\,\frac{I^{1/2}}{1+I^{1/2}} + 0{\cdot}25\,c_{\mathrm{Cl^-}} - 0{\cdot}07\,(c_{\mathrm{Cl^-}} - c_{\mathrm{H^+}}). \quad (92)$$

A comparison between the experimental values of $f_{\mathrm{H,Cl}}$ and those calculated according to (92) is given in Table XXIV. The agreement is remarkably good, especially as the ionic strength in some solutions exceeds

0·25. For the solutions containing $LaCl_3$ the activity coefficient is given similarly by

$$\left.\begin{aligned}\log_{10} f_{\mathrm{H,Cl}} &= -0{\cdot}50\,\frac{I^{1/2}}{1+I^{1/2}} + \tfrac{1}{2}\lambda_{\mathrm{H,Cl}}c_{\mathrm{Cl}^-} \\ &\quad + \tfrac{1}{2}\lambda_{\mathrm{H,Cl}}c_{\mathrm{H}^+} + \tfrac{1}{2}\lambda_{\mathrm{La,Cl}}c_{\mathrm{La}^{+++}} \\ &= -0{\cdot}50\,\frac{I^{1/2}}{1+I^{1/2}} + 0{\cdot}25\,c_{\mathrm{Cl}^-} \\ &\quad - 0{\cdot}04\,(c_{\mathrm{Cl}^-} - c_{\mathrm{H}^+}),\end{aligned}\right\} \quad . \quad . \quad . \quad (93)$$

TABLE XXIV.

Activity coefficient of HCl in mixtures of HCl and $BaCl_2$ from data of Randall and Breckenbridge[34] at 25° C.

Composition of solution.			I.	$I^{\frac{1}{2}}$.	$f_{\mathrm{H,Cl}}$ theoretical.	$f_{\mathrm{H,Cl}}$ experimental.
m_{Cl^-}.	m_{H^+}.	$m_{\mathrm{Ba}^{++}}$.				
·0500	·0375	·00625	·0563	·237	·823	·824
·1000	·0750	·0125	·1125	·336	·790	·789
·2000	·1500	·0250	·2250	·474	·768	·763
·0500	·0250	·0125	·0625	·250	·815	·811
·1000	·0500	·0250	·1250	·354	·778	·778
·2000	·1000	·0500	·2500	·500	·752	·752
·0500	·0125	·01875	·0688	·262	·805	·797*
·1000	·0250	·0375	·1375	·371	·767	·766
·2000	·0500	·0750	·2750	·524	·738	·738
·0500	·0050	·0225	·0725	·269	·800	·797
·1000	·0100	·0450	·1450	·381	·760	·759
·2000	·0200	·0900	·2900	·538	·729	·729

* The inaccuracy of this experimental value is obvious from the authors' own plot of their data.

if we assume the value 0·50 for $\lambda_{\mathrm{La,Cl}}$. The comparison between the experimental and calculated values of $f_{\mathrm{H,Cl}}$ is given in Table XXV. Again the agreement is remarkably good, even at ionic strengths exceeding considerably 0·1. Unfortunately an independent value for the interaction coefficient $\lambda_{\mathrm{La,Cl}}$ is not available. The

value 0·22 assumed for $\lambda_{Ba,Cl}$ agrees with the electrometric measurements of Lucasse[28], who used barium amalgam electrodes, within the probable accuracy of these measurements.

9. *Application to Ions of Weak Electrolyte.*

It is only recently that accurate and reliable methods have been used for determining the dissociation constant

TABLE XXV.

Activity coefficient of HCl in mixtures of HCl and $LaCl_3$ from data of Randall and Breckenbridge[34] at 25° C.

Composition of solution.			I.	$I^{\frac{1}{2}}$.	$f_{H,Cl}$ theo-retical.	$f_{H,Cl}$ experi-mental.
m_{Cl^-}.	m_{H^+}.	$m_{La^{+++}}$.				
·0500	·0375	·00417	·0625	·250	·817	·818
·1000	·0750	·00834	·1250	·354	·783	·782
·2000	·1500	·01680	·2500	·500	·760	·756
·0500	·0250	·00833	·0750	·274	·802	·811
·1000	·0500	·01667	·1500	·387	·765	·771
·2000	·1000	·03334	·3000	·548	·740	·738
·0500	·0125	·0125	·0875	·296	·787	·794
·1000	·0250	·0250	·1750	·418	·749	·754
·2000	·0500	·0500	·3500	·592	·720	·724

of a weak electrolyte. As an example we may quote the work of Harned and Ehlers[21] on the dissociation constant of acetic acid. By electromotive force measurements of cells of the type

$$Ag \mid AgCl \mid \text{Solution of } HAc + NaAc + NaCl \mid H_2, Pt$$

they obtained values for the product $m_{H^+}m_{Cl^-}\gamma_{H^+}\gamma_{Cl^-}$ in each such solution. Knowing the values of m_{HAc}, m_{Ac^-}, and m_{Cl^-} from the composition of the solution, they were thus able to compute values of the product

$$m_{H^+}m_{Ac^-}\gamma_{H^+}\gamma_{Cl^-}/m_{HAc},$$

which they denote by K′. Now the thermodynamic dissociation constant K of acetic acid is defined by

$$\frac{m_{H^+}\, m_{Ac^-}\gamma_{H^+}\gamma_{Ac^-}}{m_{HAc}\gamma_{HAc}} = K, \quad . \quad . \quad . \quad . \quad (94)$$

where γ_{HAc} denotes the activity coefficient of the undissociated acetic acid. It follows that K is related to K′ by

$$K = K' \frac{\gamma_{Ac^-}}{\gamma_{Cl^-}\gamma_{HAc}} \quad . \quad . \quad . \quad . \quad . \quad (95)$$

or

$$\log K = \log K' + \log \frac{\gamma_{Ac^-}}{\gamma_{Cl^-}} - \log \gamma_{HAc}. \quad . \quad . \quad (96)$$

As the acetate and chloride ions have the same electric charge, $\log \frac{\gamma_{Ac^-}}{\gamma_{Cl^-}}$ will in dilute solution be proportional to the salt concentration, and as the undissociated molecule is electrically neutral, $\log \gamma_{HAc}$ will also in dilute solution be proportional to the salt concentration. Hence, by a linear extrapolation of log K′ an accurate value is obtained for log K. The value thus obtained for K by Harned and Ehlers is exactly the same as that obtained by McInnes and Schedlovsky [29] by means of conductivity measurements. This remarkable agreement is strong confirmation of both the accuracy of the experimental work and the correctness of the treatment of it in both cases.

Although the method just described yields an accurate value of the thermodynamic constant K, it does not give a method of distinguishing between the two terms $\log \frac{\gamma_{Ac^-}}{\gamma_{Cl^-}}$ and $\log \gamma_{HAc}$, by which log K differs from log K′. According to our theory, provided the solutions are sufficiently dilute, the value of $\log \frac{\gamma_{Ac^-}}{\gamma_{Cl^-}}$ is given by

$$\log_{10} \frac{\gamma_{Ac^-}}{\gamma_{Cl^-}} = \tfrac{1}{2} c_{Na^+} \{\lambda_{Na,\,Ac} - \lambda_{Na,\,Cl}\}, \quad . \quad . \quad (97)$$

and so can be computed provided we know the values of the interaction coefficients $\lambda_{Na,\,Ac}$ and $\lambda_{Na,\,Cl}$. The latter is obtained directly by freezing-point measure-

ments on solutions of NaCl. The value of the former can also be determined experimentally by the following method. Freezing-point measurements are made on, for example, the following solutions :—

(1) 0·1 M NaAc + 0·010 M HAc,

(2) 0·1 M NaAc + 0·005 M HAc,

(3) 0·1 M NaAc + 0·001 M HAc.

By a simple extrapolation we could then calculate a theoretical value for what would be the freezing-point of tenth molal sodium acetate in the absence of hydrolysis. From this we can calculate directly the required value of the interaction coefficient $\lambda_{Na,\,Ac}$. It is to be hoped that freezing-point measurements of this type will be made, as at present we have no data whatever for the activity coefficients of the ions of weak electrolytes.

In a recent paper[17] is described a study of the sulfonphthalein indicator bromothymol blue in primary-secondary phosphate buffers. The acid (yellow) form A^- of this indicator has a single negative charge and the basic (blue) form B^{--} has a double negative charge. The thermodynamic equilibrium between the indicator and the buffer is given in dilute solution by

$$\frac{m_{B^{--}}\, m_{H_2PO_4^-}}{m_{A^-}\, m_{HPO_4^{--}}} = K \frac{\gamma_{A^-}\, \gamma_{HPO_4^{--}}}{\gamma_{B^{--}}\, \gamma_{H_2PO_4^-}} \quad . \quad . \quad . \quad . \quad (98)$$

As the only cation present in considerable quantity in the solutions used was Na^+, according to our present theory we have

$$\log_{10} \frac{\gamma_{A^-}\gamma_{HPO_4^{--}}}{\gamma_{B^{--}}\gamma_{H_2PO_4^-}} = \tfrac{1}{2} c_{Na^+} \{\lambda_{Na,\,A} - \lambda_{Na,\,B} + \lambda_{Na,\,HPO_4} - \lambda_{Na,\,H_2PO_4}\}, \quad . \quad . \quad . \quad (99)$$

and so

$$\log \frac{m_{B^{--}}\, m_{H_2PO_4^-}}{m_{A^-}\, m_{HPO_4^{--}}} = \log K + \tfrac{1}{2} c_{Na^+} \{\lambda_{Na,\,A} - \lambda_{Na,\,B} + \lambda_{Na,\,HPO_4} - \lambda_{Na,\,H_2PO_4}\}. \quad (100)$$

Our theory, therefore, predicts that

$$\log m_{B^{--}}\, m_{H_2PO_4^-} / m_{A^-}\, m_{HPO_4^{--}}$$

should be linear in the equivalent concentration. This was completely confirmed by the experimental measurements. This is of interest as showing that the blue form B^{--} of the sulfonphthalein indicator behaves similarly to any other bivalent anion, in spite of the rather considerable distance between the two negative charges on the ion.

10. *Individual Ionic Activity Coefficients.*

It has been pointed out elsewhere [14] that the activity coefficient of an individual ion is a conception without any thermodynamic significance. In every solution an arbitrary value may be assigned to the activity coefficient of some one ionic species, and then values assigned to those of the other ionic species so as to lead to the correct values of the mean activity coefficients of the electrolytes. It is only the latter that are measurable. There is thus an infinite number of sets of ionic activity coefficients all equally in agreement with experiment, and the choice between them is merely a matter of convention. In the range of concentration in which our theory is valid the formulæ for the mean activity coefficients suggest a very simple convention for defining individual ionic activity coefficients. For the activity coefficient f_R of a cation R we write

$$\log_{10} f_R = -0{\cdot}50 \frac{z_R^2 I^{1/2}}{1+I^{1/2}} + \sum_X \lambda_{R,X} C_X \quad . \quad . \quad . \quad (101)$$

Similarly for the activity coefficient f_X of an anion X we write

$$\log_{10} f_X = -0{\cdot}50 \frac{z_X^2 I^{1/2}}{1+I^{1/2}} + \sum_R \lambda_{R,X} C_R \quad . \quad . \quad . \quad (102)$$

By combining (101) and (102) we obtain formula (52) for the mean activity coefficient $f_{R,X}$ of the electrolyte (R, X), thus showing that the convention suggested is a permissible one. This convention leads to a particularly simple result for a solution containing only a single binary electrolyte. According to (102) we obtain

$$\log_{10} f_R = \log_{10} f_X = \log_{10} f_{R,X}$$
$$= -0{\cdot}50 \frac{z^2 I^{1/2}}{1+I^{1/2}} + \lambda_{R,X} C,$$

the two ionic activity coefficients being equal to each other and to the mean activity coefficient of the electrolyte. No alternative convention could lead to a simpler result.

References.

(1) Adams, J. Am. Chem. Soc. xxxvii. p. 481 (1915).
(2) Bjerrum, Proc. 7th Int. Cong. Chem. x. (1909).
(3) Bjerrum, *Z. El. Chem.* xxiv. p. 325 (1918) : *Z. Phys. Chem.* civ. p. 406 (1923).
(4) Bjerrum, *Kgl. Danske Vid. Selsk., Mat.-Fys. Medd.* vii. (9) (1926).
(5) Brönsted, J. Am. Chem. Soc. xliv. p. 877 (1922).
(6) Brönsted, J. Am. Chem. Soc. xliv. p. 938 (1922).
(7) Brönsted, J. Am. Chem. Soc. xlv. p. 2898 (1923).
(8) Carmody, J. Am. Chem. Soc. liv. p. 188 (1932).
(9) Debye and Hückel, *Phys. Z.* xxiv. p. 185 (1923). Debye, *Phys. Z.* xxv. p. 97 (1924).
(10) Fowler, 'Statistical Mechanics,' Cambridge Univ. Press (1929), Formula (488).
(11) Gronwall, Proc. Nat. Acad. Sci. xiii. p. 198 (1927). Gronwall, La Mer, and Sandved, *Phys. Z.* xxix. p. 358 (1928).
(12) Guggenheim, J. Phys. Chem. xxxiv. p. 1751 (1930).
(13) Guggenheim, Proc. Roy. Soc. A. cxxxv. p. 181 (1932).
(14) Guggenheim, J. Phys. Chem. xxxiii. p. 842 (1929).
(15) Guggenheim, Rep. of Scandinavian Science Congress, Copenhagen (1929), p. 298.
(16) Guggenheim, 'Modern Thermodynamics,' Methuen (1933).
(17) Guggenheim and Schindler, J. Phys. Chem. xxxviii. p. 543 (1934).
(18) Güntelberg, *Z. Phys. Chem.* cxxiii. p. 199 (1926).
(19) Hall and Harkins, J. Am. Chem. Soc. xxxviii. p. 2658 (1916).
(20) Harkins and Roberts, J. Am. Chem. Soc. xxxviii. p. 2676 (1916).
(21) Harned and Ehlers, J. Am. Chem. Soc. liv. p. 1350 (1932) ; lv. p. 652 (1933).
(22) Hovorka and Rodebush, J. Am. Chem. Soc. xlvii. p. 1614 (1925).
(23) Hückel, *Phys. Zeit.* xxvi. p. 93 (1925).
(24) Karagunis, Hawkinson, and Damköhler, *Z. Phys. Chem.* A, cli. p. 433 (1930).
(25) Lewis, G. N., J. Am. Chem. Soc. xxx. p. 668 (1908).
(26) Lewis, G. N., and Randall, J. Am. Chem. Soc. xliii. p. 1112 (1921).
(27) Lewis, G. N., and Randall, 'Thermodynamics,' McGraw Hill Book Co. (1923).
(28) Lucasse, J. Am. Chem. Soc. xlvii. p. 743 (1925).
(29) MacInnes and Schedlowsky, J. Am. Chem. Soc. liv. p. 1429 (1932).
(30) Milner, Phil. Mag. xxiii. p. 551 (1912).
(31) Müller, *Phys. Zeit.* xxviii. p. 324 (1927) ; xxix. p. 78 (1928).
(32) Onsager, Chem. Rev. xiii. p. 73 (1933).
(33) Pike and Nonhebel, Phil. Mag. l. p. 723 (1925).
(34) Randall and Breckenbridge, J. Am. Chem. Soc. xlix. p. 1435 (1927).
(35) Randall and Scott, J. Am. Chem. Soc. xlix. p. 647 (1927).
(36) Randall and Vanselow, J. Am. Chem. Soc. xlvi. p. 2418 (1924).
(37) Randall and Young, J. Am. Chem. Soc. l. p. 989 (1928).
(38) Scatchard, Jones, and Prentiss, J. Am. Chem. Soc. liv. p. 2690 (1932).
(39) Scatchard and Prentiss, J. Am. Chem. Soc. liv. p. 2696 (1932) lv. p. 4355 (1933).
(40) Washburn, *Zeit. Phys. Chem.* lxxiv. p. 537 (1910).

LI. *Path and Stability of a Local Vortex moving round a Corner.* (Third paper.) *By* ATSUSHI MIYADZU, *Assistant Professor of Hydraulics and Hydrodynamics, Tohoku Imperial University, Sendai, Japan* *.

I. SUPPLEMENT TO FORMER PAPERS.

IN my former paper † it was concluded that the stability for a small deviation of a vortex from the equilibrium position is neutral with respect to the region having only a single straight boundary. Since, however, by the same process as adopted for equation (12), but with another condition for equilibrium, equation (13) can be analyzed into

$$\frac{d\xi}{dt}=\frac{U}{Y_0}\eta \quad \text{and} \quad \frac{d\eta}{dt}=0,$$

it follows that

$$\xi=\xi_0+\frac{U}{Y_0}\eta_0 t,\ \eta=\eta_0,$$

where ξ_0 and η_0 denote the initial displacements in reference to Cartesian coordinates and t the usual period of time. Then as ξ varies with the time unless η_0 vanishes, the conclusion has to be modified in a different form, and one such that the stability is neutral only for the deviation in a direction parallel to the boundary but unstable for that in any other direction. This conclusion is equally applicable to a finite deviation as well as to the small one assumed here for the sake of simplifying the treatment, as is evidently understood from the result of the investigation of velocity components.

A similar supplement is needed also for the discussion of the stability of a vortex dealt with in my second paper ‡.

By putting $n=3$ in equation (19) we first obtain

$$L=0,\ M=0,\ N=81U\rho_0^7,\ \text{and}\ K=0;$$

then from (15)

$$\frac{d\xi}{dt}=0,\ \frac{d\eta}{dt}=81U\rho_0^7\xi;$$

* Communicated by the Author.

† A. Miyadzu, "Path and Stability of a Local Vortex moving round a Corner," Phil. Mag. xvi. pp. 553–562 (Sept. 1933).

‡ A. Miyadzu, "Path and Stability of a Local Vortex moving round a Corner" (Second paper), Phil. Mag. xvii. pp. 1010–1023 (May 1934).

and finally, by integrating them, the expressions

$$\xi=\xi_0,\ \eta=\eta_0+81\mathrm{U}\rho_0{}^7\xi_0 t,$$

where ξ and η denote the component displacements from the position of equilibrium along the radius vector and perpendicular to it. Hence it must be concluded that the equilibrium is neutral for a small deviation in a transverse direction, while it is unstable for that in any other direction. This characteristic is also capable of being readily proved to exist by merely observing the paths of a vortex in the neighbourhood of position P shown in fig. 6 *b*.

II. A Vortex maintained in a Flow of a Finite Breadth.

The problems considered in former papers were exclusively concerned with a domain bounded by two straight lines the inserted angle of which is π/n. This domain is suitable for practical use from the point that the concave or the convex side of a corner can be taken into consideration at will by simply regarding n as being greater or less than unity. The conclusions, however, will require some amendment when they are applied to the case of a complicated boundary, as is frequently met with in the problems of hydraulics. From this point of view the present writer proposes to add here the general results relative to a domain between parallel lines in addition to his second paper, for the complexity of the boundary composed of straight lines is, in general, due to a special combination of both corners and parallel lines, and, accordingly, we may to some extent infer the results by making use of the particular conclusions relating to such simpler domains as were selected as an auxiliary case even when a direct deduction for a given complicated domain may be either impossible or too complicated for practical calculation.

Let figs. 1 *a* and 1 *b* represent the t- and z-planes, respectively, with the correspondence shown by their notations; then we get

$$\frac{dz}{dt}=\frac{\mathrm{H}}{\pi}\frac{1}{t+1},\quad z=\frac{\mathrm{H}}{\pi}\log(t+1),\quad .\ .\ .\quad (1)$$

while the expressions w and w_v are the same as those given in my second paper. The relation, with special

reference to this domain, has, after some tedious evaluation, been determined as follows :—

$$-u_t+iv_t=\left(\frac{dw_v}{dt}\right)_{t=t_0}=\left(\frac{d\mathrm{F}}{dt}\right)_{t=t_0}+\frac{i\Gamma}{2\pi}\left[\frac{1}{(t_0-\bar{t}_0)}-\frac{1}{2(t_0-1)}\right].$$

Fig. 1 *a*.

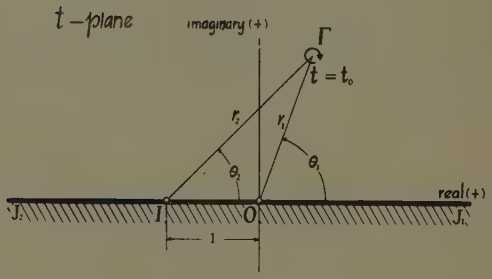
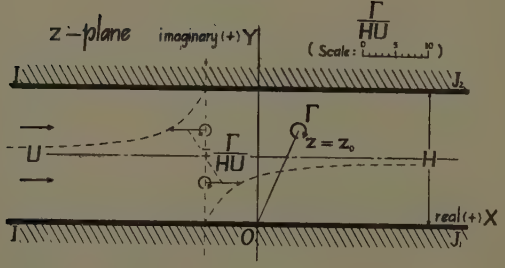


Fig. 1 *b*.



Then we get

$$\left.\begin{aligned}-u_t&=\frac{\partial \mathrm{I}}{\partial y}+\frac{\Gamma(x+1)^2}{4\pi y[(x+1)^2+y^2]},\\ v_t&=\frac{\partial \mathrm{I}}{\partial x}-\frac{\Gamma(x+1)}{4\pi[(x+1)^2+y^2]},\end{aligned}\right\}\quad\ldots\quad(2)$$

provided that

$$\left(\frac{d\mathrm{F}}{dt}\right)_{t=t_0}=\frac{d\mathrm{F}(t_0)}{dt_0},\ \mathrm{F}(t_0)=\mathrm{R}+i\mathrm{I},\ \text{and}\ \ t_0=x+iy.$$

From (2) we can obtain the general expression of the path, by a process like that used in my second paper, as

$$\frac{\Gamma}{8\pi}\log\left[y^2/\{(x+1)^2+y^2\}\right]+\mathrm{I}=\mathrm{C}, \quad . \quad . \quad . \quad (3)$$

where C is an integration constant.

In fig. 1 *a*

$$(x+1)^2+y^2=r_2^2 \text{ and } y^2=r_2^2\sin^2\theta_2\,;$$

then equation (3) can be rewritten as

$$\frac{\Gamma}{4\pi}\log\sin\theta_2+\mathrm{I}=\mathrm{C}$$

or

$$\frac{\Gamma}{4\pi}\log\sin(\pi\mathrm{Y}/\mathrm{H})+\mathrm{I}=\mathrm{C} \quad . \quad . \quad . \quad . \quad (4)$$

by putting $z=\mathrm{X}+i\mathrm{Y}$ in equation (1); this is a general expression of the path of a vortex maintained in the main flow of any type expressed by $\mathrm{F}(t)$.

The velocity components are

$$\left.\begin{aligned} u_x &= -\frac{\partial \mathrm{I}}{\partial \mathrm{Y}} - \frac{\Gamma}{4\mathrm{H}}\cot(\pi\mathrm{Y}/\mathrm{H}), \\ v &= \frac{\partial \mathrm{I}}{\partial \mathrm{X}}. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (5)$$

Equations (4) and (5) are to the present domain what equations (2) and (4) in second paper are to the previous one.

As an example let us assume here a uniform main flow for later consideration, and the general results reduce to

path;

$$\frac{\Gamma}{4\pi}\log\sin(\pi\mathrm{Y}/\mathrm{H})-\mathrm{UY}=\mathrm{C} \quad \text{or} \quad \mathrm{Y}=\text{constant}$$

velocity components;

$$\left.\begin{aligned} u_x &= \mathrm{U}-\frac{\Gamma}{4\mathrm{H}}\cot\left(\frac{\pi\mathrm{Y}}{\mathrm{H}}\right) \\ v_x &= 0 \end{aligned}\right\} \quad \text{for } 0<\mathrm{Y}<\mathrm{H},$$

where U denotes a uniform velocity of the main flow taking place in a positive direction along a real axis in fig. 1 *b*.

The condition for equilibrium becomes, by $u_z=0$,

$$\Gamma=4HU \tan (\pi Y/H).$$

Since U is a positive constant in the above equation Γ is positive or negative according as $0<Y<H/2$ or $H/2<Y<H$. If Y increases from 0 to H/2, Γ increases from 0 to $+\infty$, but it decreases in magnitude from ∞ to 0 as Y increases further from H/2 to H. Then we can deduce the following conclusions :—

(1) A vortex with a clockwise circulation can be in a state of equilibrium when at a position nearer to the boundary at the right-hand side, and a vortex with a counter-clockwise circulation can be in equilibrium when nearer to the boundary at the left-hand side, towards the under stream of the main flow respectively, and the nearer its situation to the boundary the less the strength of circulation.

(2) When there is no main flow a vortex is in a state of equilibrium midway between the two parallel boundaries, without regard to the rotational direction of its circulation.

(3) The stability of a vortex at equilibrium is neutral for a deviation parallel to the boundary and unstable for that in any other direction, as may be easily understood in the same manner as before.

For $0<Y<H/2$.

(4) A vortex with a clockwise circulation moves in the direction of or in that against the main flow, according as the strength of its circulation is less or greater than $4HU \tan (\pi Y/H)$, and is in equilibrium when it is equal to $4HU \tan (\pi Y/H)$.

(5) A vortex with a counter-clockwise circulation moves always in the same direction as the main flow irrespective of the degree of strength of circulation.

For $Y=H/2$.

(6) A vortex is always carried away by the main flow with the uniform velocity U without regard to the rotational direction and the strength of its circulation.

For $H/2<Y<H$.

(7) A similar result to that in (5) is observed in the case of a vortex with a clockwise circulation and to that in (4) in the case of one with a counter-clockwise circulation in so far as the argument is concerned with the degree of strength of circulation.

III. A Vortex maintained in a Flow having a complicated Straight Boundary.

A vortex maintained in a flow taking place inside a complicated domain bounded by straight lines can also be treated by the common general process. Let the upper half of the fundamental plane t be conformably represented on any area bounded by straight lines in the z-plane, and the relation dz/dt be known; then, by a similar process as that adopted in my second paper, we have

$$w=\mathrm{F}(t)-\frac{i\Gamma}{2\pi}\log\frac{t-t_0}{t-t_0}, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$w_0=w+\frac{i\Gamma}{2\pi}\log(z-z_0), \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and

$$-u_t+iv_t=\left[\frac{d\mathrm{F}(t)}{dt}\right]_{t=t_0}+\frac{i\Gamma}{2\pi}\frac{1}{t_0-t_0}+\frac{i\Gamma}{2\pi}\left[\frac{1}{z-z_0}\frac{dz}{dt}-\frac{1}{t-t_0}\right]_{\substack{t=t_0\\z=z_0}}.$$

Now it can be pointed out that the indeterminate form may in general be evaluated in the form

$$\left[\frac{1}{z-z_0}\frac{dz}{dt}-\frac{1}{t-t_0}\right]_{\substack{t=t_0\\z=z_0}}=\left[\frac{d^2z}{dt^2}\Big/\frac{dz}{dt}\right]_{\substack{t=t_0\\z=z_0}}.$$

Then we get

$$-u_t+iv_t=\left[\frac{d\mathrm{F}(t)}{dt}\right]_{t=t_0}+\frac{i\Gamma}{2\pi}\frac{1}{t_0-t_0}+\frac{i\Gamma}{4\pi}\left[\frac{d^2z}{dt^2}\Big/2\frac{dz}{dt}\right]_{\substack{t=t_0\\z=z_0}}, \quad . \quad . \quad . \quad (8)$$

and

$$-u_z+iv_z=(-u_t+iv_t)\left[\frac{dt}{dz}\right]_{\substack{t=t_0\\z=z_0}}. \quad . \quad . \quad (9)$$

If the relation dz/dt is established regarding the domain under consideration the motion of a vortex, maintained

in a main flow of any type expressed by $F(t)$, which takes place in this domain may be dealt with by direct deduction from these results.

As to the equation of path we can deduce it by the same process as adopted before or by the determination of Routh's stream function given by M. Lagally*, but the examination of path is omitted in what follows, since the numerical calculation became too complicated to be performed for that purpose.

Let us treat the subject with reference to the domains commonly taken into consideration in hydraulics, yet left unrevealed in their details.

IV. A Vortex maintained in a Flow with Finite Expansion.

The correspondence between the planes of t and z in fig. 2 is established by the relation

$$\frac{dz}{dt}=\frac{m\mathrm{H}}{\pi}\left(\frac{t+b}{t}\right)^{\frac{n-1}{n}}\frac{1}{t+a}, \quad . \quad . \quad . \quad . \quad (10)$$

where b and a are positive real constants, a being greater than b, connected by

$$n>1, \quad \left(\frac{a}{a-b}\right)^{\frac{n-1}{n}}=m, \quad . \quad . \quad . \quad . \quad (11)$$

H being a smaller breadth of channel and m the ratio of divergence. Then by equations (8) and (9) we have

$$-u_t+iv_t=\left[\frac{d\mathrm{F}(t)}{dt}\right]_{t=t_0}+\frac{i\Gamma}{2\pi}\frac{1}{t_0-t_0}-\frac{i\Gamma}{4\pi}\left[\frac{n-1}{n}\frac{b}{t_0(t_0+b)}+\frac{1}{t_0+a}\right]. \quad (12)$$

$$-u_z+iv_z=\frac{\pi}{m\mathrm{H}}\left(\frac{t_0}{t_0+b}\right)^{\frac{n-1}{n}}(t_0+a)[-u_t+iv_t]. \quad . \quad (13)$$

Let us here treat further a vortex maintained in a diverging main flow due to a sudden expansion of the passage, and assume the ratio of divergence in accordance

* M, Lagally, "Transformation ebener Wirbelprobleme," *Math. Zeit.* 10 (1921).

with the examples in my former paper * to be 3. Then, putting $b=2$ for the sake of convenience of treatment as well as $n=2$ and $m=3$ in (10) and (11), we obtain

$$a=9/4, \quad \frac{dz}{dt}=\frac{3H}{\pi}\frac{\sqrt{t+2}}{\sqrt{t(t+9/4)}},$$

Fig. 2 *a*.

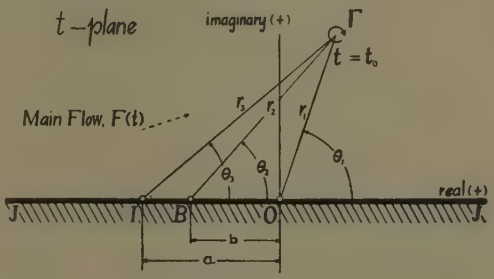
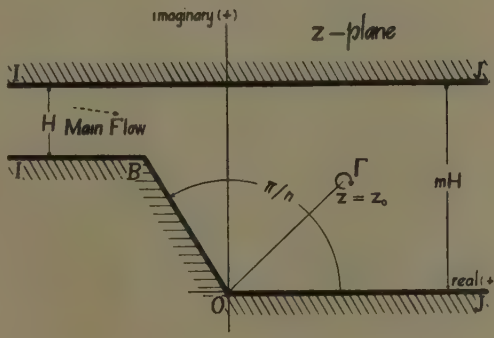


Fig. 2 *b*.



and accordingly, integrating this,

$$z=\frac{3H}{\pi}\left[\log\{t+1+\sqrt{t(t+2)}\}-\frac{1}{3}\log\frac{3\sqrt{t+2}+\sqrt{t}}{3\sqrt{t+2}-\sqrt{t}}\right]. \quad (14)$$

* A. Miyadzu, "On the Solution of the Potential Flow for an Ideal Fluid in Two Dimensions," Technol. Rep. Tohoku Imp. Univ. x. no. 4 (1932).

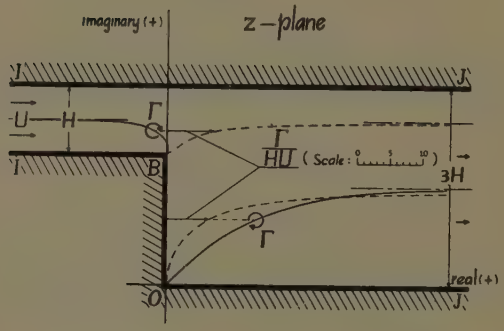
If U denotes a uniform velocity of the main flow at I (fig. 3) we may put

$$F(t) = -\frac{HU}{\pi}\log(t+9/4);$$

then, introducing this into (12), we obtain

$$-u_t+iv_t = -\frac{HU}{\pi}\frac{1}{t_0+9/4}+\frac{i\Gamma}{2\pi}\left[\frac{1}{t_0-\bar{t}_0}-\frac{t_0(t_0+2)+t_0+9/4}{2t_0(t_0+2)(t_0+9/4)}\right]. \quad (15)$$

Fig. 3.



Hence, putting

$$t_0 = r_1 e^{i\theta_1}, \quad t_0+2 = r_2 e^{i\theta_2}, \quad \text{and} \quad t_0+9/4 = r_3 e^{i\theta_3},$$

we have

$$\left.\begin{aligned} u_t &= \frac{HU}{\pi r_3}\cos\theta_3+\frac{\Gamma}{4\pi}\left[\frac{1}{r_3}\sin\theta_3+\frac{1}{r_1 r_2}\sin(\theta_1+\theta_2)-\frac{1}{r_1}\sin\theta_1\right], \\ v_t &= \frac{HU}{\pi r_3}\sin\theta_3-\frac{\Gamma}{4\pi}\left[\frac{1}{r_3}\cos\theta_3+\frac{1}{r_1 r_2}\cos(\theta_1+\theta_2)\right]. \end{aligned}\right\} \quad (16)$$

Leaving out the path, which is too complicated to be determined for numerical calculation, we will ascertain

the effect of the boundary merely on the equilibrium of a vortex.

From (16) one condition for equilibrium is obtained as

$$\cos(\theta_1+\theta_2-\theta_3)=0, \quad . \quad . \quad . \quad . \quad . \quad (17)$$

from which

$$\theta_1+\theta_2-\theta_3=\pi/2 \quad \text{or} \quad 3\pi/2, \quad (18\,a), (18\,b)$$

which can be rewritten with the geometrical relations between the triple polar coordinates shown in fig. 2 *a* as follows :—

$$16r_1r_2\sin\theta_3 \pm r_3[16r_3\cos 2\theta_3-40\cos\theta_3]\pm 9=0, \quad (19)$$

where the positive or negative sign must be used corresponding to (18 *a*) or (18 *b*).

On the other hand, another condition is

$$\frac{\Gamma}{\mathrm{HU}}=\frac{4r_1r_2\sin\theta_3}{r_1r_2\cos\theta_3+r_3\cos(\theta_1+\theta_2)}. \quad . \quad . \quad (20)$$

In (19) and (20) r_1, r_2, θ_1, and θ_2 are functions of r_3 and θ_3 ; we can then solve r_3 for given θ_3, together with the relation between Γ and U from the above equations. The co-ordinates in the z-plane corresponding to the t-plane thus determined can, of course, be obtained by equation (14). The calculated results are shown in fig. 3.

We can now proceed to write down briefly a few simpler examples.

(1) When the smaller breadth tends to 0, the other conditions being the same (fig. 4),

$$\frac{dz}{dt}=\frac{3\mathrm{H}}{\pi}\frac{1}{\sqrt{t(t+2)}},$$

$$z=\frac{3\mathrm{H}}{\pi}\log[t+1+\sqrt{t(t+2)}],$$

and

$$u_t=\frac{3\mathrm{HU}}{\pi r_2}\cos\theta_2+\frac{\Gamma}{4\pi}\Big[\frac{1}{r_2}\sin\theta_2 + \frac{1}{r_1r_2}\sin(\theta_1+\theta_2)-\frac{1}{r_1\sin\theta_1}\Big],$$

$$v_t=\frac{3\mathrm{HU}}{\pi r_2}\sin\theta_2-\frac{\Gamma}{4\pi}\Big[\frac{1}{r_2}\cos\theta_2+\frac{1}{r_1r_2}\cos(\theta_1+\theta_2)\Big].$$

The conditions for equilibrium are

$$\cos\theta_1=0 \quad \text{or} \quad \theta_1=\pi/2 \quad \text{and} \quad \frac{\Gamma}{3\mathrm{HU}}=8\tan\theta_2,$$

which can be deduced directly from the foregoing result by putting $r_3=r_2$ and $\theta_3=\theta_2$. But it is to be remarked

Fig. 4 *a*.

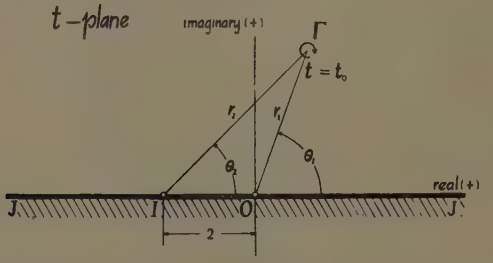
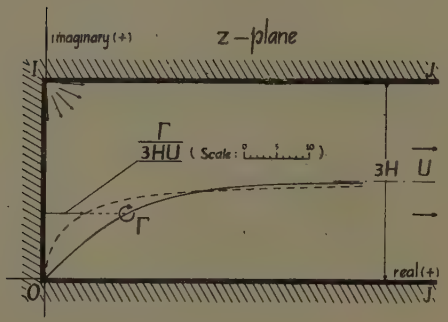


Fig. 4 *b*.



here that the notation U denotes a uniform velocity of the main flow at I in a previous case, but in this case at J.

(2) When the larger breadth tends to an infinite extent, the other conditions being the same (fig. 5),

$$\frac{dz}{dt}=\frac{\mathrm{H}}{\pi}\frac{\sqrt{t}}{t+1},$$

$$z=\frac{2\mathrm{H}}{\pi}[\sqrt{t}-\arctan\sqrt{t}],$$

and

$$u_t = \frac{HU}{\pi r_2}\cos\theta_2 + \frac{\Gamma}{4\pi r_2}\left[\frac{1}{2}\sin\theta_2 - \frac{1}{2r_1}\sin(\theta_1+\theta_2) - \frac{1}{\sin\theta_2}\right],$$

$$v_t = \frac{HU}{\pi r_2}\sin\theta_2 - \frac{\Gamma}{4\pi r_2}\left[\frac{1}{2}\cos\theta_2 + \frac{1}{2r_1}\cos(\theta_1+\theta_2)\right].$$

Fig. 5 *a*.

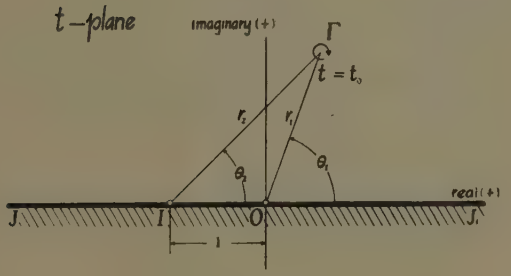
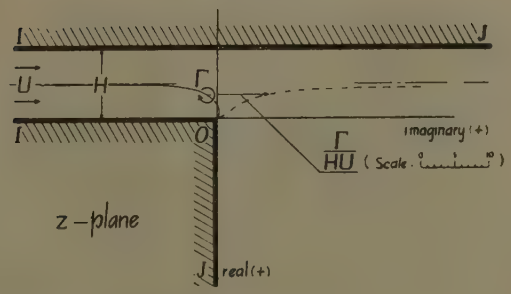


Fig. 5 *b*.



The conditions for equilibrium are

$$r_1 = -\cos\theta_1 \quad \text{and} \quad \frac{\Gamma}{HU} = \frac{8\cos\theta_1\sin\theta_2}{\cos\theta_1\cos\theta_2 + \cos(\theta_1+\theta_2)}.$$

(3) When a straight boundary tends to an infinite extent, the other conditions being the same (fig. 6),

$$\frac{dz}{dt}=\frac{2H}{\pi}\sqrt{\frac{t+1}{t}},$$

$$z=\frac{2H}{\pi}[\sqrt{t(t+1)}+\log(\sqrt{t}+\sqrt{t+1})],$$

Fig. 6 *a*.

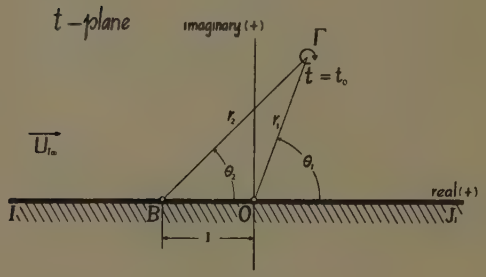
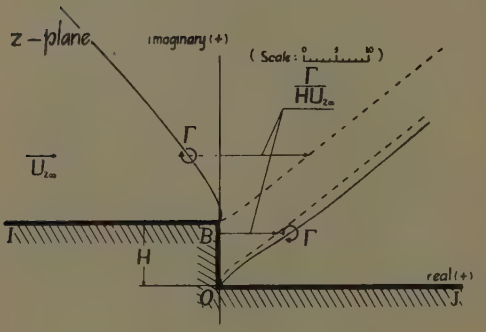


Fig. 6 *b*.



and

$$u_1=U_{1\infty}+\frac{\Gamma}{4\pi r_1}\left[\frac{1}{2r_2}\sin(\theta_1+\theta_2)-\frac{1}{\sin\theta_1}\right],$$

$$v_1=-\frac{\Gamma}{8\pi r_1 r_2}\cos(\theta_1+\theta_2).$$

The conditions for equilibrium are

$$\cos(\theta_1+\theta_2)=0,\ \text{or}\ \theta_1+\theta_2=\pi/2,\ 3\pi/2,$$

and $$\frac{\Gamma}{\mathrm{H}U_{z\infty}} = -\frac{8\tan 2\theta_1}{2+\cos 2\theta_1},$$

where $$U_{z\infty} = \frac{\pi}{2\mathrm{H}} U_{t\infty}.$$

The loci of the positions for equilibrium obtained and shown in this section all correspond to positive Γ, and the greater the strength of circulation the farther the position recedes from the nearer boundary. Then it may be concluded that (1) a vortex with a clockwise circulation maintained in a main flow with a sudden finite expansion to the right-hand side can be in the state of equilibrium at two points in a domain for a given strength of circulation, (2) while a vortex with a counter-clockwise circulation cannot be in such a state at any point.

(4) A vortex maintained in a flow with a sharp bend *.

The solution for this example is also analytically very similar to that in the original example concerning a vortex maintained in a flow with sudden expansion. The chief difference is that a must now be taken to be less than b in the relation between z and t, such that

$$\frac{dz}{dt} = \frac{m\mathrm{H}}{\pi} \frac{\sqrt{t+b}}{\sqrt{t(t+a)}},$$

and $$\left(\frac{a}{b-a}\right)^{\frac{1}{2}} = m,$$

where H is the smaller breadth of channel and m the ratio of divergence.

Putting $b=2$ and $m=3$, as before, we obtain

$$a=9/5, \quad \frac{dz}{dt} = \frac{3\mathrm{H}}{\pi} \frac{\sqrt{t+2}}{\sqrt{t(t+9/5)}}.$$

Then z is integrated as follows, relatively to the coordinates in fig. 7*b*:

$$z = \frac{3\mathrm{H}}{\pi}\left[\log\{t+1+\sqrt{t(t+2)}\} - \frac{1}{3}\arctan\left\{\frac{4t+9}{3\sqrt{t(t+2)}}\right\}\right] + \frac{\mathrm{H}}{2}. \quad . \quad . \quad (21)$$

* For the sake of simplifying the description only one case in which the contained angle of a concave corner is $\pi/2$ has been written down here as an example.

On the other hand, putting

$$t_0=r_1e^{i\theta_1},\ t_0+2=r_2e^{i\theta_2},\ \text{and}\ t_0+\frac{9}{5}=r_3e^{i\theta_3},$$

Fig. 7*a*.

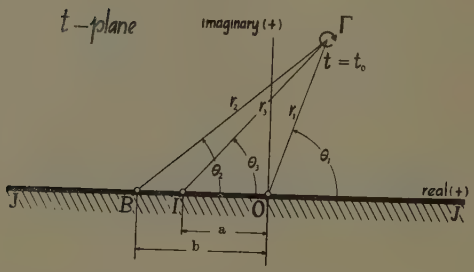
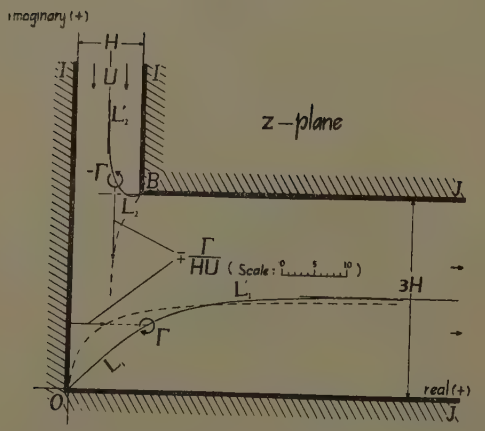


Fig. 7*b*.



we have the same equations with respect to u_t and v_t as those in equation (16); consequently the same expressions for the conditions for equilibrium are

$$\cos(\theta_1+\theta_2-\theta_3)=0, \quad . \quad . \quad . \quad . \quad . \quad (17)$$

$$\frac{\Gamma}{\mathrm{H}\bar{\mathrm{U}}} = \frac{4r_1r_2 \sin\theta_3}{r_1r_2 \cos\theta_3 + r_3 \cos(\theta_1+\theta_2)}. \quad . \quad . \quad (20)$$

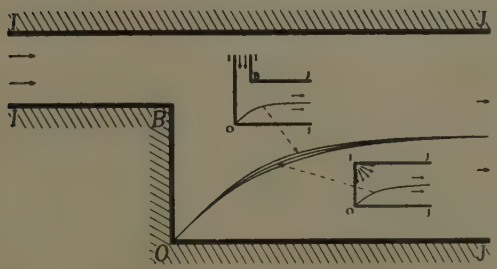
But as a solution of (17) suitable for this case we must choose the only one applicable, viz.,

$$\theta_1+\theta_2-\theta_3=\pi/2, \quad . \quad . \quad . \quad . \quad . \quad (18\,a)$$

as may be easily understood by inspection of the arrangements of polar coordinates. Moreover this can be rewritten in the form

$$r_1r_2 \sin\theta_2 + r_3(r_2 \cos 2\theta_2 - 2\cos\theta_2)=0, \quad . \quad (22)$$

Fig. 8.



which can, of course, be modified into an implicit function between r_2 and θ_2 by making use of the geometrical relations between the triple polar coordinates; from this two r_2's are found corresponding to each θ_2. Hence we have obtained two curves of the loci of positions for equilibrium such as $\mathrm{L_1L_1'}$ and $\mathrm{L_2L_2'}$ in fig. 7 *b*. (20) gives positive or negative Γ for $\mathrm{L_1L_1'}$ or $\mathrm{L_2L_2'}$, each increasing in magnitude from 0 to an infinite amount, as traced along it from a corner; it may then be concluded that, (1) a vortex with a clockwise circulation can be in equilibrium on a curve issuing from a concave corner, and a vortex with a counter-clockwise circulation can be so on a curve issuing from a convex corner; and, (2) the greater the strength of circulation becomes in degree the farther the position for equilibrium recedes from the nearer boundary.

V. Concluding Remarks.

The particular results shown in section IV., when taken together, will give the detailed data for discussion of the effects of the inlet portion on the change of the equilibrium position of a vortex in the neighbourhood of a concave corner, where the diverging main flow is used to accompany a local vortex in an ordinary state of flow ; fig. 8 has been shown for this purpose. Yet, so far as the argument is concerned with a qualitative result, deduced by each example separately, it is sufficiently explained without any analytical treatment merely by referring to the conclusions *, given below, in the case of such a simple and fundamental example as that in my first paper ; for this purpose the conclusions relating to a vortex in a uniform main flow with a finite breadth may be taken into consideration as for a supplementary use.

A similar argument will also to some extent be applicable to the path of a vortex, notwithstanding that the direct deduction of the result for it may be either impossible or too complicated for numerical calculation. In the foregoing treatment our attention has therefore been arbitrarily confined to the problem of equilibrium.

In conclusion, the writer wishes to express his grateful acknowledgments to Prof. O. Miyagi for his guidance and encouragement, and also to express his thanks to Mr. T. Tanabe, who assisted him in numerical calculations.

Sendai.
July 12th, 1934.

---

* Supplementary conclusions for equilibrium of a vortex dealt with in my first paper :—

(1) A vortex can be in the state of equilibrium when it has a clockwise circulation to a main flow taking place in a direction having the region under consideration on the left-hand side of the " boundary " as traced.

(2) The locus of the positions for equilibrium is a line bisecting the inserted angle of the domain.

(3) The greater the strength of circulation becomes the farther the position on the locus recedes from the " boundary."

In applying these conclusions to the consideration of a vortex maintained in a flow taking place in a complicated domain bounded by straight lines, " boundary " in (1) and (3) above must, of course, be replaced by " boundary forming the nearer corner."

LII. *Induced Radioactivity and Particle Emission.*

By F. H. Newman, *D.Sc., Professor of Physics, and* H. J. Walke, *M.Sc., Demonstrator in Physics, University College, Exeter* *.

1. Introduction.

MANY elements display induced radioactivity after bombardment by one or other of the four agents of transmutation, viz., α-particles, diplons, protons, and neutrons. In certain cases positive results have been obtained by some observers and not by others, but this may signify simply a weaker bombarding stream, or a less sensitive detector in the apparatus of the latter. In many cases the observed action is complex, as the heavier elements of even atomic number possess several isotopes, and many different reactions can occur as the result of interaction between the bombarding particles and the various nuclei. The type of interaction also depends upon the energy of the incident particle; for example, Feather † has concluded that the photographs of nuclear disintegration which he obtained by bombarding nitrogen with neutrons suggested that in some cases protons, rather than α-particles, were emitted. This has been confirmed by Kurie ‡, whose results show the track of an ejected particle, which has a density of ionization much less than that corresponding to an α-particle, and is probably a proton or diplon.

The problem is further complicated by the fact that the radioactive isotope produced may give rise by β-ray disintegration to a second unstable nucleus, so that a form of radioactive series may be observed on account of these double transformations. It is thus apparent that the problem is a complex one.

In the present paper we consider possible radioactive isotopes and indicate reactions whereby they may be produced by suitable nuclear transmutations. While we postulate these β-radioactive isotopes, it is to be noted that we do not suggest that all the reactions will be confirmed experimentally. The type of disintegration

* Communicated by the Authors.

† Proc. Roy. Soc. A, cxxxvi. p. 709 (1933).

‡ Phys. Rev. xlv. p. 904 (1934).

observed depends upon the energy of the bombarding neutrons. In addition, since Fermi's results * indicate that there is no nuclear potential barrier for neutrons, so that they can penetrate all nuclei, the probability of interaction between neutrons and various isotopes depends upon the abundance of such isotopes, and thus some of the reactions will not be observed, on account of the small abundance of the bombarded nuclei.

Three types of nuclear action under neutron bombardment are possible. Fermi has separated chemically β-radioactive isotopes of atomic number Z$-$2, Z$-$1, and Z from elements of atomic number Z, and although there is as yet little evidence of the separation of two such isotopes, formed by the bombardment of one element, the results of Kurie † and of Bjerge and Westcott ‡ indicate that this can be observed.

2. β-radioactive Isotopes of Atomic Number below Oxygen.

Walke § has suggested that the nuclear structure of the elements of atomic number less than oxygen, as indicated by their nuclear disintegrations, is as follows. Elements of even atomic number consist of the maximum number of α-particles and a neutron (He_2^5 is stable, though a rare isotope, on this hypothesis). Those of odd atomic number contain the maximum number of α-particles, a diplon, and in some cases a loosely-bound neutron. We now suggest that in this group missing isotopes of elements of even atomic number, containing two neutrons, are unstable and β-radioactive, transmuting to the next stable isotope of odd atomic number containing a diplon, and that the missing, unstable isotopes of odd atomic number, consisting of α-particles, a diplon, and two neutrons, are also β-radioactive, transmuting to the next stable α-particle configuration.

In the following discussion we indicate first the radioactive isotope, and then the possible ways in which it can be produced.

* *Ricerca Scientifica*, v. pp. 1, 283, 330, 452 (1934).
† *Loc. cit.*
‡ 'Nature,' cxxxiv. p. 176 (1934).
§ Phil. Mag. xvii. p. 793 (1934).

(a) *Elements of Even Atomic Number.*

Helium.

$$He_2^6 \quad \{[\alpha]+2n\} \rightarrow Li_3^6\{[\alpha]+D\}+\overset{\nearrow}{\beta}.$$

$$He_2^5+n \rightarrow He_2^6,$$

$$Li_3^6+n \rightarrow He_2^6+\overset{\nearrow}{p}.$$

$$Be_4^9+n \rightarrow He_2^6+\overset{\nearrow}{\alpha}.$$

Of these reactions, the first cannot be observed experimentally, since He_2^5 has not yet been detected. Moreover, beryllium is easily disintegrated by α-particles with neutron emission, so that in the third reaction electrons should be observed when beryllium is bombarded to produce neutrons. No mention has yet been made of the appearance of the electrons, so we conclude that the second mode of formation of He_2^6 is most likely.

Beryllium.

$$Be_4^{10} \quad \{[2\alpha]+2n\} \rightarrow B_5^{10}\{[2\alpha]+D\}+\overset{\nearrow}{\beta}.$$

$$Be_4^9+n \rightarrow Be_4^{10},$$

$$B_5^{10}+n \rightarrow Be_4^{10}+\overset{\nearrow}{p},$$

$$C_6^{13}+n \rightarrow Be_4^{10}+\overset{\nearrow}{\alpha}.$$

The third reaction would not be detected, as C_6^{13} exists in very small quantity. In view of the large number of isotopes of some of the heavier atoms—formed, most probably, by the addition of neutrons to the basic structure of one of the lighter isotopes—it must be concluded that neutron capture without the emission of nuclear particles, other than electrons if the resulting nucleus is missing, is possible with all elements. This capture process, in the case of beryllium, is only possible with neutrons of low energy, so that the most likely method of forming radioactive beryllium is to bombard boron with neutrons, when the isotope will be produced following the emission of protons.

Carbon.

$$C_6^{14} \quad \{[3\alpha]+2n\} \rightarrow N_7^{14}\{[3\alpha+D\}+\overset{\nearrow}{\beta}.$$

$$C_6^{13}+n \rightarrow C_6^{14},$$

$$N_7^{14}+n \rightarrow C_6^{14}+\overset{\nearrow}{p},$$

$$O_8^{17}+n \rightarrow C_6^{14}+\overset{\nearrow}{\alpha}.$$

Of these methods of formation, the first and third are impracticable, since C_6^{13} and O_8^{17} exist in such small quantities, and, therefore, C_6^{14} can only be produced by bombarding nitrogen with neutrons. This reaction was probably photographed by Kurie *, the slight β-radioactivity under neutron bombardment being due to the formation of radioactive carbon.

(b) *Elements of Odd Atomic Number.*

Lithium.

$$Li_3^8 \quad \{[\alpha]+D+2n\} \rightarrow Be_4^8\{[2\alpha]\}+\overset{\nearrow}{\beta}.$$

$$Li_3^7+n \rightarrow Li_3^8,$$

$$Be_4^8+n \rightarrow Li_3^8+\overset{\nearrow}{p},$$

$$B_5^{11}+n \rightarrow Li_3^8+\overset{\nearrow}{\alpha}.$$

The first and third methods of production are possible, but the second is unlikely, since Be_4^8 is so unstable that it probably disintegrates into two α-particles and a neutron when bombarded with neutrons of sufficient energy to cause disintegration. With low-energy neutrons Be_4^9 will be formed by capture. In addition, the small abundance of Be_4^8 precludes the second reaction. The first method of formation represents simple neutron capture, and, probably, low-energy neutrons are required. Since we have already suggested that Li_3^6, bombarded with neutrons, emits protons and transmutes to the radioactive He_2^6, we should expect two periods of radioactive

* *Loc. cit.*

decay associated with the bombardment of lithium with neutrons.

The observed emission of α-particles from carbon, nitrogen, oxygen, fluorine, and neon suggests that the third reaction is also likely, so that when boron is bombarded with neutrons two decay periods should be observed, one due to the formation of Be_4^{10} by emission of protons from the lighter isotope, and the other arising from the formation of Li_3^8 by the emission of α-particles from the heavier isotope.

Boron.

$$B_5^{12} \quad \{[2\alpha]+D+2n\}\rightarrow C_6^{12}\{[3\alpha]\}+\overset{\nearrow}{\beta}.$$

$$B_5^{11}+n\rightarrow B_5^{12},$$

$$C_6^{12}+n\rightarrow B_5^{12}+\overset{\nearrow}{p},$$

$$N_7^{15}+n\rightarrow B_5^{12}+\overset{\nearrow}{\alpha}.$$

Of these methods of production the second is unlikely to be detected, except in a few stereoscopic photographs, since C_6^{12} is very stable, and only disintegrates when bombarded with high-energy neutrons, α-particles being emitted. N_7^{15} exists in very small quantity, and hence B_5^{12} can most likely be produced by simple neutron capture, the reaction probably taking place with neutrons of low energies.

Nitrogen.

$$N_7^{16} \quad \{[3\alpha]+D+2n\}\rightarrow O_8^{16}\{[4\alpha]\}+\overset{\nearrow}{\beta}.$$

$$N_7^{15}+n\rightarrow N_7^{16},$$

$$O_8^{16}+n\rightarrow N_7^{16}+\overset{\nearrow}{p},$$

$$F_9^{19}+n\rightarrow N_7^{16}+\overset{\nearrow}{\alpha}.$$

The most probable method of producing radioactive nitrogen is from fluorine, according to the third reaction. In support of this suggested reaction it may be mentioned

that Harkins, Gans, and Newson * have photographed the emission of α-particles from fluorine bombarded with neutrons, and Fermi † has detected β-radioactivity with fluorine under neutron bombardment. O_8^{16} is only disintegrable with high-speed neutrons, α-particles being emitted, and N_8^{15} is so scarce that the first and second reactions are not likely to be detected.

3. β-RADIOACTIVE ISOTOPES OF ELEMENTS FROM OXYGEN TO SULPHUR.

In the group of elements from oxygen to sulphur the heaviest stable nuclei of even atomic number contain two neutrons in addition to the maximum number of α-particles, while the elements of odd atomic number contain the maximum number of α-particles, a diplon, and a loosely-bound neutron. We postulate that the missing, unstable isotopes of even atomic number—containing three neutrons—spontaneously disintegrate by emitting β-rays, transmuting to the stable isotope of the next element of odd atomic number. The missing, unstable isotopes of odd atomic number, consisting of a diplon and two neutrons, in addition to the maximum number of α-particles, transmute by β-radioactivity to the next stable α-particle configuration.

(a) *Elements of Even Atomic Number.*

Oxygen.

The missing, unstable isotope of oxygen is O_8^{19}, which disintegrates thus :—

$$O_8^{19} \quad \{[4\alpha]+3n\} \rightarrow F_9^{19}\{[4\alpha]+D+n\}+\overset{\nearrow}{\beta}.$$

It may be produced by the following reactions :—

$$O_8^{18}+n \rightarrow O_8^{19},$$

$$F_9^{19}+n \rightarrow O_9^{19}+\overset{\nearrow}{p},$$

$$Ne_{10}^{22}+n \rightarrow O_8^{19}+\overset{\nearrow}{\alpha}.$$

* Phys. Rev. xliv. p. 945 (1933).
† *Loc. cit.*

Of these reactions the first and third are not likely to be detected owing to the scarcity of O^{18} and Ne^{22}, but the second method is practicable.

Neon.

$$Ne_{10}^{23} \quad \{[5\alpha]+3n\} \rightarrow Na_{11}^{23}\{[5\alpha]+D+n\}+\overset{\nearrow}{\beta}.$$

$$Ne_{10}^{22}+n \rightarrow Ne_{10}^{23},$$

$$Na_{11}^{23}+n \rightarrow Ne_{10}^{23}+\overset{\nearrow}{p},$$

$$Mg_{12}^{26}+n \rightarrow Ne_{10}^{23}+\overset{\nearrow}{\alpha}.$$

The second and third reactions are most likely to be observed experimentally, since Ne_{10}^{22} exists in small abundance. The most suitable reaction is the second one, sodium having a single isotope. The variation of its activity under neutron bombardment, as the energy of the neutrons is varied, could be tested.

Magnesium.

$$Mg_{12}^{27} \quad \{[6\alpha]+3n\} \rightarrow Al_{13}^{27}\{[6\alpha]+D+n\}+\overset{\nearrow}{\beta}.$$

$$Mg_{12}^{26}+n \rightarrow Mg_{12}^{27},$$

$$Al_{13}^{27}+n \rightarrow Mg_{12}^{27}+\overset{\nearrow}{p},$$

$$Si_{14}^{30}+n \rightarrow Mg_{12}^{27}+\overset{\nearrow}{\alpha}.$$

All of these reactions are possible, but the second one is the most promising, since the magnesium and silicon isotopes are unlikely to be very abundant, and any radioactive effect, due to nuclear actions with the more abundant isotopes of these elements, may mask the β-ray emission from Mg^{26} and Si^{30}.

Silicon.

$$Si_{14}^{31} \quad \{[7\alpha]+3n\} \rightarrow P_{15}^{31}\{[7\alpha]+D+n\}+\overset{\nearrow}{\beta}.$$

$$Si_{14}^{30}+n \rightarrow Si_{14}^{31},$$

$$P_{15}^{31}+n \rightarrow Si_{14}^{31}+\overset{\nearrow}{p},$$

$$S_{16}^{34}+n \rightarrow Si_{14}^{31}+\overset{\nearrow}{\alpha}.$$

The second method of production is the most probable, and has been observed by Fermi. The first one is possible, and probably occurs in the evolution of the elements, but would be difficult to observe experimentally. S^{34}_{16} is very scarce, and this precludes the third method.

Sulphur.

$$S^{35}_{16} \quad \{[8\alpha]+3n\} \rightarrow Cl^{35}_{17}\{[8\alpha]+D+n\}+\overset{\nearrow}{\beta}.$$

$$S^{34}_{16}+n \rightarrow S^{35}_{16},$$

$$Cl^{35}_{17}+n \rightarrow S^{35}_{16}+\overset{\nearrow}{p},$$

$$Ar^{38}_{18}+n \rightarrow S^{35}_{16}+\overset{\nearrow}{\alpha}.$$

As with the other elements of this group, the most probable method of formation is the second one, since S^{34} and Ar^{38} exist in such small abundance that the detection of the radioactive sulphur would be almost impossible in the presence of other, more probable reactions with the abundant isotopes of these elements.

(b) *Elements of Odd Atomic Number.*

Fluorine.

$$F^{20}_{9} \quad \{[4\alpha]+D+2n\} \rightarrow Ne^{20}_{10}\{[5\alpha]\}+\overset{\nearrow}{\beta}.$$

$$F^{19}_{9}+n \rightarrow F^{20}_{9},$$

$$Ne^{20}_{10}+n \rightarrow F^{20}_{9}+\overset{\nearrow}{p},$$

$$Na^{23}_{11}+n \rightarrow F^{20}_{9}+\overset{\nearrow}{\alpha}.$$

The first method of production is by simple neutron capture, the bombarding neutrons having low energy. In connexion with the second method, Harkins, Gans, and Newson photographed stereoscopically the disintegration of neon by neutrons, α-particles being emitted, corresponding to the formation of O^{17}. Thus, with sodium, Na^{23}, three β-ray, unstable isotopes should be produced by neutron bombardment, viz., Na^{24}, F^{20}, and Ne^{23}, corresponding to simple neutron capture, α-particle, and proton emission, respectively.

Sodium.

$$Na_{11}^{21} \quad \{[5\alpha]+D+2n\} \rightarrow Mg_{12}^{24}\{[6\alpha]\}+\overset{\nearrow}{\beta}.$$

$$Na_{11}^{23}+n \rightarrow Na_{11}^{24},$$

$$Mg_{12}^{24}+n \rightarrow Na_{11}^{24}+\overset{\nearrow}{p},$$

$$Al_{13}^{27}+n \rightarrow Na_{11}^{24}+\overset{\nearrow}{\alpha}.$$

All three methods of production are possible, and may be observed experimentally.

Aluminium.

$$Al_{13}^{28} \quad \{[6\alpha]+D+2n\} \rightarrow Si_{14}^{28}\{[7\alpha]\}+\overset{\nearrow}{\beta}.$$

$$Al_{13}^{27}+n \rightarrow Al_{13}^{28},$$

$$Si_{14}^{28}+n \rightarrow Al_{13}^{28}+\overset{\nearrow}{p}.$$

$$P_{15}^{31}+n \rightarrow Al_{13}^{28}+\overset{\nearrow}{\alpha}.$$

The second reaction has been observed by Fermi, and, in addition, Bjerge and Westcott * found that under neutron bombardment phosphorus gives rise to two radioactive isotopes which decay with periods of 2·5 hours and 2·5 minutes respectively. As the period of radioactive aluminium due to proton emission from silicon is also 2·5 minutes, we conclude that both the second and third reactions have been experimentally observed, the active product of short life from phosphorus being Al^{28}. The equality of these transformation periods is definite evidence in favour of our hypothesis, since it proves that a radioactive isotope can be produced from two elements.

Phosphorus.

$$P_{15}^{32} \quad \{7[\alpha]+D+2n\} \rightarrow S_{16}^{32}\{[8\alpha]\}+\overset{\nearrow}{\beta}.$$

$$P_{15}^{31}+n \rightarrow P_{15}^{32},$$

$$S_{16}^{32}+n \rightarrow P_{15}^{32}+\overset{\nearrow}{p},$$

$$Cl_{17}^{35}+n \rightarrow P_{15}^{32}+\overset{\nearrow}{\alpha}.$$

* *Loc. cit.*

As proton emission has been detected from phosphorus bombarded with neutrons it would appear that the first method of production is less probable than the other two.

The case of phosphorus is interesting, since from the given reactions (neglecting the neutron-capture process, which we regard as probable with all nuclei) we suggest that two periods of decay could be observed by bombarding the element with neutrons of energy sufficient to cause disintegration corresponding to the emission of protons and α-particles, viz.,

$$P_{15}^{31}+n\rightarrow Si_{14}^{31}+\nearrow p,$$
$$P_{15}^{31}+n\rightarrow Al_{13}^{28}+\nearrow \alpha.$$

This has been confirmed by Bjerge and Westcott *, who varied the energy of the bombarding neutrons and found that phosphorus exhibited the two forms of activity mentioned. They found, however, that only the long-life activity was exhibited when phosphorus was bombarded with neutrons arising from the reaction $Be_4^9+D_1^2$, whereas the two decay periods were present when the "beryllium α-particle" neutron-source was used. Thus, as phosphorus is a single isotope, we have definite evidence in support of our hypothesis that the formation of more than one β-radioactive isotope, from the same parent nucleus, is possible under bombardment by neutrons of suitable energies. Additional confirmation is afforded by the recent work of Bjerge and Westcott †, as they have observed the formation of Na^{24} from Na^{23} by simple neutron capture. Since Fermi had formed this isotope, Na^{24}, from magnesium and aluminium according to the reactions

$$Mg_{12}^{24}+n\rightarrow Na_{11}^{24}+\nearrow p,$$
$$Al_{13}^{27}+n\rightarrow Na_{11}^{24}+\nearrow \alpha,$$

we see that all three methods of formation of the unstable isotope, which we postulated, have been confirmed experimentally. In addition, they have observed two

* *Loc. cit.*
† 'Nature,' cxxxiv. p. 286 (1934).

β-radioactive isotopes with fluorine and sodium. According to our views three reactions are possible, and we anticipate that with increased refinement of technique all three periods of decay will be found corresponding to simple neutron capture, neutron capture with proton emission, and neutron capture with α-particle emission.

4. β-RADIOACTIVE ISOTOPES OF THE ELEMENTS FROM CHLORINE TO ZINC.

As regards the elements of atomic number greater than that of sulphur, it is impossible to formulate definite rules regarding the mass numbers of the β-radioactive isotopes other than as follows. Among the elements of even atomic number the isotope, of mass greater by unity than the heaviest isotope in the mass spectrum, is β-radioactive, and so is a "missing, unstable" isotope—one unit less in mass than the last stable isotope. In a few cases, which will be indicated, there are other missing isotopes that are spontaneously β-radioactive, transmuting to elements of higher atomic number. With elements of odd atomic number the isotopes heavier by unit mass than the heavier stable isotopes are missing, and in such cases we suggest that they are β-radioactive. These isotopes, and the possible nuclear reactions by means of which they can be formed, will now be considered.

(a) *Elements of Even Atomic Number.*

Argon.

$$Ar^{39}_{18} \rightarrow K^{39}_{19} + \overset{\nearrow}{\beta}.$$

$$Ar^{38}_{18} + n \rightarrow Ar^{39}_{18},$$

$$K^{39}_{19} + n \rightarrow Ar^{39}_{18} + \overset{\nearrow}{p},$$

$$Ca^{42}_{20} + n \rightarrow Ar^{39}_{18} + \overset{\nearrow}{\alpha}.$$

Of these reactions the first and third are unlikely to be detected, since the stable isotopes, Ar^{38} and Ca^{42}, exist only in small abundance. Hence, if radioactive argon, Ar^{39}, is to be detected, potassium, K^{39}, must be bombarded with neutrons, when the unstable nucleus will be formed with proton emission.

Argon.

$$\mathrm{Ar}_{18}^{41} \rightarrow \mathrm{K}_{19}^{41} + \overset{\nearrow}{\beta}.$$

$$\mathrm{Ar}_{18}^{40} + n \rightarrow \mathrm{Ar}_{18}^{41},$$

$$\mathrm{K}_{19}^{41} + n \rightarrow \mathrm{Ar}_{18}^{41} + \overset{\nearrow}{p},$$

$$\mathrm{Ca}_{20}^{44} + n \rightarrow \mathrm{Ar}_{18}^{41} + \overset{\nearrow}{\alpha}.$$

The first method of production is the most important, since K^{41} and Ca^{44} only exist in small abundance.

Calcium.

$$\mathrm{Ca}_{20}^{45} \rightarrow \mathrm{Sc}_{21}^{45} + \overset{\nearrow}{\beta}.$$

$$\mathrm{Ca}_{20}^{44} + n \rightarrow \mathrm{Ca}_{20}^{45},$$

$$\mathrm{Sc}_{21}^{45} + n \rightarrow \mathrm{Ca}_{20}^{45} + \overset{\nearrow}{p},$$

$$\mathrm{Ti}_{22}^{48} + n \rightarrow \mathrm{Ca}_{20}^{45} + \overset{\nearrow}{\alpha}.$$

The second and third methods of production are the most promising, since Ca^{44} exists in small quantities.

Titanium.

$$\mathrm{Ti}_{22}^{51} \rightarrow \mathrm{V}_{23}^{51} + \overset{\nearrow}{\beta},$$

$$\mathrm{Ti}_{22}^{50} + n \rightarrow \mathrm{Ti}_{22}^{51},$$

$$\mathrm{V}_{23}^{51} + n \rightarrow \mathrm{Ti}_{22}^{51} + \overset{\nearrow}{p},$$

$$\mathrm{Cr}_{24}^{54} + n \rightarrow \mathrm{Ti}_{22}^{51} + \overset{\nearrow}{\alpha}.$$

The abundance of Ti^{50} and Cr^{54} is such that the most probable method of producing the radioactive titanium isotope is by bombarding vanadium with neutrons of appropriate energy; protons will be emitted and the unstable nucleus formed.

Chromium.

$$\mathrm{Cr}_{24}^{55} \rightarrow \mathrm{Mn}_{25}^{55} + \overset{\nearrow}{\beta}.$$

$$\mathrm{Cr}_{24}^{54} + n \rightarrow \mathrm{Cr}_{24}^{55},$$

$$\mathrm{Mn}_{25}^{55} + n \rightarrow \mathrm{Cr}_{24}^{55} + \overset{\nearrow}{p}.$$

Of these modes of formation the second is the more probable.

The next elements in the periodic table, iron and cobalt, have probably more isotopes than at present determined, and, therefore, a discussion of the radioactive isotopes of iron will be postponed until further evidence of its isotopic nature is available.

Nickel.

$$Ni_{28}^{63} \rightarrow Cu_{29}^{63} + \overset{\nearrow}{\beta}.$$

$$Ni_{28}^{62} + n \rightarrow Ni_{28}^{63},$$

$$Cu_{29}^{63} + n \rightarrow Ni_{28}^{63} + \overset{\nearrow}{p},$$

$$Zn_{30}^{66} + n \rightarrow Ni_{28}^{63} + \overset{\nearrow}{\alpha}.$$

Ni^{62} exists in slight abundance, but Zn^{66} is fairly plentiful, so that the second and third reactions will proceed with neutrons of appropriate energy.

Nickel.

$$Ni_{28}^{65} \rightarrow Cu_{29}^{65} + \overset{\nearrow}{\beta}.$$

$$Ni_{28}^{64} + n \rightarrow Ni_{28}^{65},$$

$$Cu_{29}^{65} + n \rightarrow Ni_{28}^{65} + \overset{\nearrow}{p},$$

$$Zn_{30}^{68} + n \rightarrow Ni_{28}^{65} + \overset{\nearrow}{\alpha},$$

and, as with the lighter, unstable nickel isotope, the second and third reactions are the most probable.

Germanium.

$$Ge_{32}^{75} \rightarrow As_{33}^{75} + \overset{\nearrow}{\beta}.$$

$$Ge_{32}^{74} + n \rightarrow Ge_{32}^{75},$$

$$As_{33}^{75} + n \rightarrow Ge_{32}^{75} + \overset{\nearrow}{p},$$

$$Se_{34}^{78} + n \rightarrow Ge_{32}^{75} + \overset{\nearrow}{\alpha}.$$

The first and second reactions are probable, the first occurring when the energy of the bombarding neutrons is small. Although the third method of formation is possible, Se^{78} may also capture a neutron to form the β-radioactive isotope Se^{79}, which is spontaneously transformed to Br^{79}_{35}.

The missing, unstable isotope, Ge^{77}_{32}, is also β-radioactive, but the transformation

$$Ge^{77}_{32} \rightarrow As^{77}_{33} + \overset{\nearrow}{\beta}$$

does not produce a stable isotope, since As^{77} is missing. There is, however, a stable selenium isotope of mass 77, so that we have in this case two succeeding β-ray transformations from Ge^{77}, viz.,

$$Ge^{77}_{32} \rightarrow As^{77}_{33} + \overset{\nearrow}{\beta}$$

and then

$$As^{77}_{33} \rightarrow Se^{77}_{34} + \overset{\nearrow}{\beta}.$$

We shall encounter several of these double transformations in the next section.

(b) *Elements of Odd Atomic Number.*

In view of the probable relationship between the radioactive isotopes of chlorine and potassium, and the spontaneous β-radioactivity of potassium, discussion of the missing isotopes of these elements will be omitted for the present. Hence the next β-radioactive isotope is scandium.

Scandium.

$$Sc^{46}_{21} \rightarrow Ti^{46}_{22} + \overset{\nearrow}{\beta}.$$

$$Sc^{45}_{21} + n \rightarrow Sc^{46}_{21},$$

$$Ti^{46}_{22} + n \rightarrow Sc^{46}_{21} + \overset{\nearrow}{p}.$$

The small abundance of Ti^{46} indicates that the unstable scandium isotope can only be produced in very small amount. Formation by simple neutron capture is possible, provided that the bombarding neutrons are of small energy.

Vanadium.

$$V_{23}^{52} \rightarrow Cr_{24}^{52} + \overset{\nearrow}{\beta}.$$

$$V_{23}^{51} + n \rightarrow V_{23}^{52},$$

$$Cr_{24}^{52} + n \rightarrow V_{23}^{53} + \overset{\nearrow}{p},$$

$$Mn_{25}^{55} + n \rightarrow V^{52} + \overset{\nearrow}{\alpha}.$$

All three methods of production are probable, provided that the bombarding neutrons are of appropriate energy. In all processes of simple neutron capture, without disintegration, the energy of the bombarding neutrons should be low. In general the experimental work performed to date has been with neutrons of such high energy that disintegration, rather than simple capture, is favoured.

Manganese.

$$Mn_{25}^{56} \rightarrow Fe_{26}^{56} + \overset{\nearrow}{\beta}.$$

$$Mn_{25}^{55} + n \rightarrow Mn_{25}^{56},$$

$$Fe_{26}^{56} + n \rightarrow Mn_{25}^{56} + \overset{\nearrow}{p},$$

$$Co_{27}^{59} + n \rightarrow Mn_{25}^{56} + \overset{\nearrow}{\alpha}.$$

Mn^{56} affords further evidence that the same radioactive isotope may be produced from two elements, since Fermi has detected radioactive manganese when iron and cobalt are bombarded with neutrons. The unstable isotope is formed according to the reactions given above.

Cobalt.

$$Co_{27}^{60} \rightarrow Ni_{28}^{60} + \overset{\nearrow}{\beta}.$$

$$Co_{27}^{59} + n \rightarrow Co_{27}^{60},$$

$$Ni_{28}^{60} + n \rightarrow Co_{27}^{60} + \overset{\nearrow}{p},$$

$$Cu_{29}^{63} + n \rightarrow Co_{27}^{60} + \overset{\nearrow}{\alpha}.$$

Copper.

$$Cu_{29}^{64} \rightarrow Zn_{30}^{64} + \overset{\nearrow}{\beta}.$$

$$Cu_{29}^{63} + n \rightarrow Cu_{29}^{64},$$

$$Zn_{29}^{64} + n \rightarrow Cu_{29}^{64} + \overset{\nearrow}{p}.$$

Copper.

$$Cu_{29}^{66} \rightarrow Zn_{30}^{66} + \overset{\nearrow}{\beta}.$$

$$Cu_{29}^{65} + n \rightarrow Cu_{29}^{66},$$

$$Zn_{30}^{66} + n \rightarrow Cu_{29}^{66} + \overset{\nearrow}{p},$$

$$Ga_{31}^{69} + n \rightarrow Cu_{29}^{66} + \overset{\nearrow}{\alpha}.$$

Confirmation of some of these suggested reactions has recently been given by Bjerge and Westcott *, who observed the formation of radioactive copper from copper and zinc.

5. Successive β-radioactive Changes.

In the last section it was suggested that there are two succeeding β-ray transformations associated with the unstable Ge^{77}, and two decay periods are thus possible when Ge^{76} is bombarded with neutrons of small energy. Several reactions may occur, however, when germanium is bombarded with neutrons, viz.,

$$Ge_{32}^{70} + n \rightarrow Ga_{31}^{70} + \overset{\nearrow}{p},$$

$$Ge_{32}^{72} + n \rightarrow Zn_{30}^{69} + \overset{\nearrow}{\alpha},$$

$$Ge_{32}^{74} + n \rightarrow Ge_{32}^{75},$$

$$Ge_{32}^{72} + n \rightarrow Ga_{31}^{72} + \overset{\nearrow}{p},$$

$$Ge_{32}^{74} + n \rightarrow Zn_{30}^{71} + \overset{\nearrow}{\alpha},$$

and as all of the unstable isotopes so formed are β-ray emitters, the double β-ray emission may be difficult to detect. In this case several decay periods will normally

* *Loc. cit.*

be observed, corresponding to the formation of the several radioactive isotopes, and we suggest that the number of decay periods found will depend upon the energy of the bombarding neutrons.

Other examples of double β-ray emissions are given by the following missing isotopes :—

Selenium.

$$Se_{34}^{83} \rightarrow \overset{\nearrow}{\beta} + Br_{35}^{83} \rightarrow Kr_{36}^{83} + \overset{\nearrow}{\beta},$$

produced by

$$Se_{34}^{82} + n \rightarrow Se_{34}^{83}$$

or

$$Kr_{36}^{86} + n \rightarrow Se_{34}^{83} + \overset{\nearrow}{\alpha}.$$

The first method of production is the more probable.

Zirconium.

$$Zr_{40}^{95} \rightarrow \overset{\nearrow}{\beta} + Nb_{41}^{95} \rightarrow Mo_{42}^{95} + \overset{\nearrow}{\beta}$$

and

$$Zr_{40}^{97} \rightarrow \overset{\nearrow}{\beta} + Nb_{41}^{97} \rightarrow Mo_{42}^{97} + \overset{\nearrow}{\beta},$$

the isotopes Nb^{95} and Nb^{97}, being missing, are, according to our theory, β-radioactive. The unstable zirconium isotopes could be produced thus :—

$$Zr_{40}^{94} + n \rightarrow Zr_{40}^{95}\ ; \quad Zr_{40}^{96} + n \rightarrow Zr_{40}^{97},$$

$$Mo_{42}^{98} + n \rightarrow Zr_{40}^{95} + \overset{\nearrow}{\alpha}\ ; \quad Mo_{42}^{100} + n \rightarrow Zr_{40}^{97} + \overset{\nearrow}{\alpha}.$$

The more probable method of production is that involving the disintegration of the molybdenum isotopes with α-particle emission, and we should, therefore, anticipate two successive β-ray transformations when molybdenum is bombarded with neutrons.

Ruthenium.

$$Ru_{44}^{105} \rightarrow \overset{\nearrow}{\beta} + Rh_{45}^{105} \rightarrow Pd_{46}^{105} + \overset{\nearrow}{\beta}.$$

$$Ru_{44}^{104} + n \rightarrow Ru_{44}^{105},$$

$$Pd_{46}^{108} + n \rightarrow Ru_{44}^{105} + \overset{\nearrow}{\alpha}.$$

Although the isotopic constitution of palladium has not yet been determined, there is probably an isotope of mass number 108.

Cadmium.

$$\mathrm{Cd}_{48}^{117} \rightarrow \overset{\nearrow}{\beta} + \mathrm{In}_{49}^{117} \rightarrow \mathrm{Sn}_{50}^{117} \times \overset{\nearrow}{\beta}.$$

$$\mathrm{Cd}_{48}^{116} + n \rightarrow \mathrm{Cd}_{48}^{117},$$

$$\mathrm{Sn}_{50}^{120} + n \rightarrow \mathrm{Cd}_{48}^{117} + \overset{\nearrow}{\alpha}.$$

Cd^{116} exists in very small quantity, but the most abundant tin isotope is that of mass number 120, and so it is anticipated that, when tin is bombarded with neutrons of such energy that α-particle emission occurs, two succeeding β-ray transformations will be observed.

Tellurium.

$$\mathrm{Te}_{52}^{129} \rightarrow \overset{\nearrow}{\beta} + \mathrm{I}_{53}^{129} \rightarrow \mathrm{Xe}_{54}^{129} + \overset{\nearrow}{\beta}$$

and $$\mathrm{Te}_{52}^{131} \rightarrow \overset{\nearrow}{\beta} + \mathrm{I}_{53}^{131} \rightarrow \mathrm{Xe}_{54}^{131} + \overset{\nearrow}{\beta}.$$

These unstable tellurium isotopes may be produced thus :—

$$\mathrm{Te}_{52}^{128} + n \rightarrow \mathrm{Te}_{52}^{129}\ ; \quad \mathrm{Te}_{52}^{130} + n \rightarrow \mathrm{Te}_{52}^{131},$$

or $$\mathrm{Xe}_{54}^{132} + n \rightarrow \mathrm{Te}_{52}^{129} + \overset{\nearrow}{\alpha}\ ; \quad \mathrm{Xe}_{54}^{134} + n \rightarrow \mathrm{Te}_{52}^{131} + \overset{\nearrow}{\alpha}.$$

As xenon is a gas, the amount of the appropriate isotope which could be suitably bombarded with neutrons is so small that the formation of the radioactive isotopes would only occur to a slight extent, and their detection would be difficult. However, the two most abundant tellurium isotopes are Te^{128} and Te^{130}, so that successive transformations should be observed when tellurium is bombarded with neutrons.

Xenon.

$$\mathrm{Xe}_{54}^{135} \rightarrow \overset{\nearrow}{\beta} + \mathrm{Cs}_{55}^{135} \rightarrow \mathrm{Ba}_{56}^{135} + \overset{\nearrow}{\beta}$$

and $$\mathrm{Xe}_{54}^{137} \rightarrow \overset{\nearrow}{\beta} + \mathrm{Cs}_{55}^{137} \rightarrow \mathrm{Ba}_{56}^{137} + \overset{\nearrow}{\beta}.$$

The unstable xenon isotopes may be formed by the following reactions :—

$$\mathrm{Xe}_{54}^{134} + n \rightarrow \mathrm{Xe}_{54}^{135}\ ; \quad \mathrm{Xe}_{54}^{136} + n \rightarrow \mathrm{Xe}_{54}^{137},$$

$$\mathrm{Ba}_{56}^{138} + n \rightarrow \mathrm{Xe}_{54}^{135} + \overset{\nearrow}{\alpha}.$$

The second reaction is the more promising, and barium bombarded with neutrons should show a double β-ray transformation.

Rare-earth Elements.

In view of the present lack of knowledge of the relative abundance of rare-earth isotopes it is difficult to state which of the reactions below are the most probable, and so we merely give the possible ways in which the missing isotopes might be formed.

Cerium.

$$\mathrm{Ce}_{58}^{143} \rightarrow \overset{\nearrow}{\beta} + \mathrm{Pr}_{59}^{143} \rightarrow \mathrm{Nd}_{60}^{143} + \overset{\nearrow}{\beta}.$$

$$\mathrm{Ce}_{58}^{142} + n \rightarrow \mathrm{Ce}_{58}^{143},$$

$$\mathrm{Nd}_{60}^{146} + n \rightarrow \mathrm{Ce}_{58}^{143} + \overset{\nearrow}{\alpha}.$$

Gadolinium.

$$\mathrm{Gd}_{64}^{161} \rightarrow \overset{\nearrow}{\beta} + \mathrm{Tb}_{65}^{161} \rightarrow \mathrm{Dy}_{66}^{161} + \overset{\nearrow}{\beta}.$$

$$\mathrm{Dy}_{66}^{164} + n \rightarrow \mathrm{Gd}_{64}^{161} + \overset{\nearrow}{\alpha},$$

$$\mathrm{Gd}_{64}^{160} + n \rightarrow \mathrm{Gd}_{64}^{161}.$$

Erbium.

$$\mathrm{Er}_{68}^{171} \rightarrow \overset{\nearrow}{\beta} + \mathrm{Tu}_{69}^{171} \rightarrow \mathrm{Yb}_{70}^{171} + \overset{\nearrow}{\beta}.$$

$$\mathrm{Er}_{68}^{170} + n \rightarrow \mathrm{Er}_{68}^{171},$$

$$\mathrm{Yb}_{70}^{174} + n \rightarrow \mathrm{Er}_{68}^{171} + \overset{\nearrow}{\alpha}.$$

Ytterbium.

$$\mathrm{Yb}_{70}^{177} \rightarrow \overset{\nearrow}{\beta} + \mathrm{Lu}_{71}^{177} \rightarrow \mathrm{Hf}_{72}^{177} + \overset{\nearrow}{\beta}.$$

$$\mathrm{Yb}_{70}^{176} + n \rightarrow \mathrm{Yb}_{70}^{177},$$

$$\mathrm{Hf}_{72}^{180} + n \rightarrow \mathrm{Yb}_{70}^{177} + \overset{\nearrow}{\alpha}.$$

6. β-RADIOACTIVE ISOTOPES OF THE ELEMENTS FROM ARSENIC TO PALLADIUM.

(a) *Elements of Odd Atomic Number.*

Arsenic.

$$As_{33}^{76} \rightarrow Se_{34}^{76} + \overset{\nearrow}{\beta}.$$

$$As_{33}^{75} + n \rightarrow As_{33}^{76},$$

$$Se_{33}^{76} + n \rightarrow As_{33}^{76} + \overset{\nearrow}{p},$$

$$Br_{35}^{79} + n \rightarrow As_{33}^{76} + \overset{\nearrow}{\alpha}.$$

Of these reactions the third is the most probable as Se^{76} exists in very small quantity, and the simple neutron capture is only likely to occur with neutrons of low energy.

Bromine.

$$Br_{35}^{80} \rightarrow Kr_{36}^{80} + \overset{\nearrow}{\beta}.$$

$$Br_{35}^{79} + n \rightarrow Br_{35}^{80},$$

$$Kr_{36}^{80} + n \rightarrow Br_{35}^{80} + \overset{\nearrow}{p}.$$

The first method of production is promising, although with high-energy neutrons disintegration occurs and nuclear particles are emitted, leading to the formation of other unstable isotopes such as Se^{79} (following proton emission) or As^{76} (following α-particle emission).

Bromine.

$$Br_{35}^{82} \rightarrow Kr_{36}^{82} + \overset{\nearrow}{\beta}.$$

$$Br_{35}^{81} + n \rightarrow Br_{35}^{82},$$

$$Kr_{36}^{82} + n \rightarrow Br_{35}^{82} + \overset{\nearrow}{p},$$

$$Rb_{37}^{85} + n \rightarrow Br_{35}^{82} + \overset{\nearrow}{\alpha}.$$

With neutrons of high energy value the third method of formation of this unstable bromine isotope probably occurs. The other two are possible.

In view of the spontaneous radioactivity of rubidium, consideration of this element will be deferred.

Niobium.

$$Nb^{94}_{41} \rightarrow Mo^{94}_{42} + \overset{\nearrow}{\beta}.$$

$$Nb^{93}_{41} + n \rightarrow Nb^{94}_{41},$$

$$Mo^{94}_{42} + n \rightarrow Nb^{94}_{41} + \overset{\nearrow}{p},$$

and we should, therefore, expect radioactive niobium to be produced, with proton emission, when molybdenum is bombarded with neutrons.

Although masurium has not yet been isolated in sufficient abundance for its mass spectrum to be investigated, the missing molybdenum isotopes of mass numbers 99 and 101 suggest that masurium has stable isotopes of corresponding mass numbers, so that the probable radioactive masurium isotopes are :—

Masurium.

$$Ms^{100}_{43} \rightarrow Ru^{100}_{44} + \overset{\nearrow}{\beta}; \quad Ms^{102}_{43} \rightarrow Ru^{102}_{44} + \overset{\nearrow}{\beta}.$$

produced as follows :—

$$Ms^{99}_{43} + n \rightarrow Ms^{100}_{43}; \qquad Ms^{101}_{43} + n \rightarrow Ms^{102}_{43},$$

$$Ru^{100}_{44} + n \rightarrow Ms^{100}_{43} + \overset{\nearrow}{p}; \quad Ru^{102}_{44} + n \rightarrow Ms^{102}_{43} + \overset{\nearrow}{p}.$$

$$Rh^{103}_{45} + n \rightarrow Ms^{100}_{43} + \overset{\nearrow}{\alpha}.$$

In view of the small abundance of masurium and the relatively high abundance of Ru^{99} and Ru^{101}, it is probable that masurium is itself spontaneously radioactive, the supposed stable isotopes of mass numbers 99 and 101 being β-radioactive of comparatively long life. The element illinium, of atomic number 61, may be similar in nature.

Rhodium.

$$Rh^{104}_{45} \rightarrow Pd^{104}_{46} + \overset{\nearrow}{\beta}.$$

$$Rh^{103}_{45} + n \rightarrow Rh^{104}_{45},$$

$$Pd^{100}_{46} + n \rightarrow Rh^{100}_{45} + \overset{\nearrow}{p},$$

$$Ag^{107}_{47} + n \rightarrow Rh^{104}_{45} + \overset{\nearrow}{\alpha}.$$

Since the atomic weight of palladium is 106·7, it is probable that Pd^{104} exists only in small quantity, and, therefore, the most likely method of producing radioactive rhodium is by bombarding silver with neutrons, the radioactive isotope resulting from the ejection of α-particles from the lighter silver isotope.

(b) *Elements of Even Atomic Number.*

Selenium.

$$Se^{79}_{34} \rightarrow Br^{79}_{35} + \overset{\nearrow}{\beta}; \quad Se^{81}_{34} \rightarrow Br^{81}_{35} + \overset{\nearrow}{\beta}.$$

$$Se^{78}_{34} + n \rightarrow Se^{79}_{34}; \qquad Se^{80}_{34} + n \rightarrow Se^{81}_{34},$$

$$Br^{79}_{35} + n \rightarrow Se^{79}_{34} + \overset{\nearrow}{p}; \quad Br^{81}_{35} + n \rightarrow Se^{81}_{34} + \overset{\nearrow}{p},$$

$$Kr^{82}_{36} + n \rightarrow Se^{79}_{34} + \overset{\nearrow}{\alpha}; \quad Kr^{84}_{36} + n \rightarrow Se^{81}_{34} + \overset{\nearrow}{\alpha}.$$

Bombardment of bromine with neutrons appears to be the most promising method of producing these unstable selenium isotopes.

Krypton.

$$Kr^{85}_{36} \rightarrow Rb^{85}_{37} + \overset{\nearrow}{\beta}.$$

$$Kr^{84}_{36} + n \rightarrow Kr^{85}_{36},$$

$$Rb^{85}_{37} + n \rightarrow Kr^{85}_{36} + \overset{\nearrow}{p},$$

$$Sr^{88}_{38} + n \rightarrow Kr^{85}_{36} + \overset{\nearrow}{\alpha}.$$

Of these production methods the second and third are most likely to be observed experimentally. Similarly,

Krypton.

$$Kr^{87}_{36} \rightarrow Rb^{87}_{37} + \overset{\nearrow}{\beta}.$$

$$Kr^{86}_{36} + n \rightarrow Kr^{87}_{36},$$

$$Rb^{87}_{37} + n \rightarrow Kr^{87}_{36} + \overset{\nearrow}{p}.$$

Thus, by bombarding rubidium with neutrons we should expect to observe β-radioactivity, following the ejection of protons, due to the formation of radioactive krypton,

which, being a gas, might be emitted to give a pseudo-radioactive rubidium emanation.

Strontium.

$$Sr_{38}^{89} \rightarrow Y_{9}^{89} + \overset{\nearrow}{\beta}.$$

$$Sr_{38}^{88} + n \rightarrow Sr_{38}^{89},$$

$$Y_{39}^{89} + n \rightarrow Sr_{38}^{89} + \overset{\nearrow}{p},$$

$$Zr_{40}^{92} + n \rightarrow Sr_{38}^{89} + \overset{\nearrow}{\alpha}.$$

Since Zr^{92} exists in small quantity, the most suitable method of producing radioactive strontium is by the bombardment of yttrium with neutrons.

Zirconium.

$$Zr_{40}^{93} \rightarrow Nb_{41}^{93} + \overset{\nearrow}{\beta}.$$

$$Zr_{40}^{2} + n \rightarrow Zr_{40}^{93},$$

$$Nb_{41}^{93} + n \rightarrow Zr_{40}^{93} + \overset{\nearrow}{p},$$

$$Mo_{42}^{96} + n \rightarrow Zr_{40}^{93} + \overset{\nearrow}{\alpha},$$

both disintegration reactions being probable.

Molybdenum.

$$Mo_{42}^{99} \rightarrow Ms_{43}^{99} + \overset{\nearrow}{\beta}; \quad Mo_{42}^{101} + Ms_{43}^{101} + \overset{\nearrow}{\beta}.$$

$$Mo_{42}^{98} + n \rightarrow Mo_{42}^{99}; \qquad Mo_{42}^{100} + n \rightarrow Mo_{42}^{101},$$

$$Ms_{43}^{99} + n \rightarrow Mo_{42}^{98} + \overset{\nearrow}{p}; \quad Ms_{43}^{101} + n \rightarrow Mo_{42}^{101} + \overset{\nearrow}{p},$$

$$Ru_{44}^{102} + n \rightarrow Mo_{42}^{99} + \overset{\nearrow}{\alpha}; \quad Ru_{44}^{104} + n \rightarrow Mo_{42}^{101} + \overset{\nearrow}{\alpha},$$

the radioactive molybdenum isotopes being produced from masurium and ruthenium.

Ruthenium.

$$Ru_{44}^{103} \rightarrow Rh_{45}^{103} + \overset{\nearrow}{\beta}.$$

$$Ru_{44}^{102} + n \rightarrow Ru_{44}^{103},$$

$$Rh_{45}^{103} + n \rightarrow Ru_{44}^{103} + \overset{\nearrow}{p}.$$

Palladium.

The palladium isotopes Pd^{107} and Pd^{109} are probably missing, and disintegrate spontaneously as follows :—

$$Pd_{46}^{107} \rightarrow Ag_{47}^{107} + \overset{\nearrow}{\beta}; \quad Pd_{46}^{109} \rightarrow Ag_{47}^{109} + \overset{\nearrow}{\beta}.$$

$$Pd_{46}^{106} + n \rightarrow Pd_{46}^{107}; \qquad Pd_{46}^{108} + n \rightarrow Pd_{46}^{107},$$

$$Ag_{47}^{107} + n \rightarrow Pd_{46}^{107} + \overset{\nearrow}{p}; \quad Ag_{47}^{109} + n \rightarrow Pd_{46}^{109} + \overset{\nearrow}{p},$$

$$Cd_{48}^{110} + n \rightarrow Pd_{46}^{107} + \overset{\nearrow}{\alpha}; \quad Cd_{48}^{112} + n \rightarrow Pd_{46}^{109} + \overset{\nearrow}{\alpha},$$

so that radioactive palladium may be prepared by bombarding silver, or cadmium, with neutrons of appropriate energy.

7. Induced β-radioactivity and Missing Stable Isotopes.

There are certain missing unstable isotopes, especially among the rare-earth elements, which cannot spontaneously disintegrate, according to our hypothesis, into known stable isotopes, *e. g.*, Ba_{56}^{134}, Ds_{66}^{160}, and Yb_{70}^{170}. It is noteworthy that Cd_{48}^{108} was in this class, but has recently been detected *. We predict, therefore, that these three isotopes are stable, although as yet undetected. They arise from the following missing, unstable isotopes :—

$$Cs_{55}^{134} \rightarrow Ba_{56}^{134} + \overset{\nearrow}{\beta},$$

$$Tb_{65}^{160} \rightarrow Ds_{66}^{160} + \overset{\nearrow}{\beta},$$

$$Tu_{69}^{170} \rightarrow Yb_{70}^{170} + \overset{\nearrow}{\beta}.$$

These unstable isotopes, Cs^{134}, Tb^{160}, and Tu^{170}, may be produced by simple neutron capture, *i. e.*, bombarding the elements cæsium, terbium, and thulium with neutrons of low-energy value.

In addition, we suggest radioactive series among the light elements to explain the existence of the lighter

* See Aston, ' Nature,' cxxxiv. p. 178 (1934).

isotopes of certain elements such as Kr_{36}^{78}, Sn_{50}^{112}, etc. These series effects might be observed if the radioactive parent isotope could be produced, and are to be expected following the formation of Br_{35}^{82}, Ms_{43}^{100}, Ag_{47}^{110}, In_{49}^{116}, I_{53}^{128}, Il_{61}^{148}, and Au_{79}^{206} by the processes already described, or which will be given, in this paper. In these reactions an α-ray emission occurs from a small percentage of nuclei formed in a state of excess energy. They are all of the general form

$$In_{49}^{116} \rightarrow \overset{\nearrow}{\beta} + Sn_{50}^{116} \rightarrow \overset{\nearrow}{\alpha} + Cd_{48}^{112} \rightarrow \overset{\nearrow}{\beta} + In_{49}^{112}.$$

It is questionable, however, whether these reactions could be produced to such an extent for the series effect to be followed in detail.

8. β-RADIOACTIVE ISOTOPES OF THE ELEMENTS FROM SILVER TO THE RARE EARTHS.

(a) *Elements of Even Atomic Number.*

Cadmium.

$$Cd_{48}^{115} \rightarrow In_{49}^{115} + \overset{\nearrow}{\beta}.$$

$$Cd_{48}^{114} + n \rightarrow Cd_{48}^{115},$$

$$In_{49}^{115} + n \rightarrow Cd_{48}^{115} + \overset{\nearrow}{p},$$

$$Sn_{50}^{118} + n \rightarrow Cd_{48}^{115} + \overset{\nearrow}{\alpha},$$

and we predict induced radioactivity when indium and tin are bombarded with neutrons.

Tin.

$$Sn_{50}^{123} \rightarrow Sb_{51}^{123} + \overset{\nearrow}{\beta}.$$

$$Sn_{50}^{122} + n \rightarrow Sn_{50}^{123},$$

$$Sb_{51}^{123} + n \rightarrow Sn_{50}^{123} + \overset{\nearrow}{p},$$

$$Te_{52}^{126} + n \rightarrow Sn_{50}^{123} + \overset{\nearrow}{\alpha}.$$

Tellurium.

$$Te_{52}^{127} \rightarrow I_{53}^{127} + \overset{\nearrow}{\beta}.$$

$$Te_{52}^{126} + n \rightarrow Te_{52}^{127},$$

$$I_{53}^{127} + n \rightarrow Te_{52}^{127} + \overset{\nearrow}{p},$$

$$Xe_{54}^{130} + n \rightarrow Te_{52}^{127} + \overset{\nearrow}{\alpha}.$$

The reaction suggested with iodine has not been confirmed, the experimental result with iodine under neutron bombardment being simple neutron capture to produce the radioactive I_{53}^{128}. We anticipate, however, that under bombardment by neutrons of high-energy value disintegration will occur and radioactive tellurium will be produced, following proton emission.

Xenon.

$$Xe_{54}^{133} \rightarrow Cs_{55}^{133} + \overset{\nearrow}{\beta}.$$

$$Xe_{54}^{132} + n \rightarrow Xe_{54}^{133},$$

$$Cs_{55}^{133} + n \rightarrow Xe_{54}^{133} + \overset{\nearrow}{p},$$

$$Ba_{56}^{136} + n \rightarrow Xe_{54}^{133} + \overset{\nearrow}{\alpha},$$

the second method of production being the most favoured.

Barium.

$$Ba_{56}^{139} \rightarrow La_{57}^{139} + \overset{\nearrow}{\beta}.$$

$$Ba_{56}^{138} + n \rightarrow Ba_{56}^{139},$$

$$La_{57}^{139} + n \rightarrow Ba_{55}^{139} + \overset{\nearrow}{p},$$

$$Ce_{58}^{142} + n \rightarrow Ba_{56}^{139} + \overset{\nearrow}{\alpha},$$

the first two methods of production being likely, since the cerium isotope is rare.

(b) *Elements of Odd Atomic Number.*

Silver.

$$Ag_{47}^{110} \rightarrow Cd_{48}^{110} + \overset{\nearrow}{\beta}.$$

$$Ag_{47}^{109} + n \rightarrow Ag_{47}^{110},$$

$$Cd_{48}^{110} + n \rightarrow Ag_{47}^{110} + \overset{\nearrow}{p}.$$

Indium.

$$In_{49}^{116} \rightarrow Sn_{50}^{116} + \overset{\nearrow}{\beta}.$$

$$In_{49}^{115} + n \rightarrow In_{49}^{116},$$

$$Sn_{50}^{116} + n \rightarrow In_{49}^{116} + \overset{\nearrow}{p}.$$

Antimony.

$$Sb_{51}^{122} \rightarrow Te_{52}^{122} + \overset{\nearrow}{\beta}; \quad Sb_{51}^{124} \rightarrow Te_{52}^{124} + \overset{\nearrow}{\beta}.$$

$$Sb_{51}^{121} + n \rightarrow Sb_{51}^{122}; \qquad Sb_{51}^{123} + n \rightarrow Sb_{51}^{124},$$

$$Te_{52}^{122} + n \rightarrow Sb_{51}^{122} + \overset{\nearrow}{p}; \quad Te_{52}^{124} + n \rightarrow Sb_{51}^{124} + \overset{\nearrow}{p}.$$

The most probable method of production of the above unstable isotopes is by simple neutron capture.

Iodine.

$$I_{53}^{128} \rightarrow Xe_{54}^{128} + \overset{\nearrow}{\beta}.$$

$$I_{53}^{127} + n \rightarrow I_{53}^{128},$$

$$Xe_{54}^{128} + n \rightarrow I_{53}^{128} + \overset{\nearrow}{p}.$$

In this case, also simple neutron capture is the method of production favoured, and this is in agreement with experimental evidence.

9. α-RADIOACTIVE ISOTOPES OF THE RARE-EARTH ELEMENTS.

At present the isotopic data for the rare-earth elements are incomplete, and it is difficult to discuss the likely reactions which will produce the radioactive isotopes within this class. But we have indicated that the ejection of more than one type of nuclear component from an isotope is possible, and has been observed in some cases. Hence we suggest that the β-radioactive isotopes given below can be produced by bombardment of appropriate stable isotopes with neutrons of suitable energy value. For the rare-earth isotopes, therefore, we shall merely indicate first the spontaneous radioactive transition, followed by the possible methods of production of the unstable isotope.

Lanthanum.

$$La_{57}^{140} \rightarrow Ce_{58}^{140} + \overset{\nearrow}{\beta}.$$

$$La_{57}^{139} + n \rightarrow La_{57}^{140},$$

$$Ce_{58}^{140} + n \rightarrow La_{57}^{140} + \overset{\nearrow}{p}.$$

Cerium.

$$Ce_{58}^{141} \rightarrow Pr_{59}^{141} + \overset{\nearrow}{\beta}.$$

$$Ce_{58}^{140} + n \rightarrow Ce_{58}^{141},$$

$$Pr_{59}^{141} + n \rightarrow Ce_{58}^{141} + \overset{\nearrow}{p}.$$

Praseodymium.

$$Pr_{59}^{142} \rightarrow Nd_{60}^{142} + \overset{\nearrow}{\beta}.$$

$$Pr_{59}^{141} + n \rightarrow Pr_{59}^{142},$$

$$Nd_{60}^{142} + n \rightarrow Pr_{59}^{142} + \overset{\nearrow}{p}.$$

Illinium.

$$Il_{61}^{148} \rightarrow Sm_{62}^{148} + \overset{\nearrow}{\beta}.$$

$$Il_{61}^{147} + n \rightarrow Il_{61}^{148},$$

$$Sm_{62}^{148} + n \rightarrow Il_{61}^{148} + \overset{\nearrow}{p},$$

$$Eu_{63}^{151} + n \rightarrow Il_{61}^{148} + \overset{\nearrow}{\alpha}.$$

Samarium.

$$Sm_{62}^{151} \rightarrow Eu_{63}^{151} + \overset{\nearrow}{\beta}; \quad Sm_{62}^{153} \rightarrow Eu_{63}^{153} + \overset{\nearrow}{\beta}.$$

$$Sm_{62}^{150} + n \rightarrow Sm_{62}^{151}; \qquad Sm_{62}^{152} + n \rightarrow Sm_{62}^{153},$$

$$Eu_{63}^{151} + n \rightarrow Sm_{62}^{151} + \overset{\nearrow}{p}; \quad Eu_{63}^{153} + n \rightarrow Sm_{62}^{153} + \overset{\nearrow}{p},$$

$$Gd_{64}^{154} + n \rightarrow Sm_{62}^{151} + \overset{\nearrow}{\alpha}; \quad Gd_{64}^{156} + n \rightarrow Sm_{62}^{153} + \overset{\nearrow}{\alpha}.$$

Europium.

$$Eu_{63}^{152} \rightarrow Gd_{64}^{152} + \overset{\nearrow}{\beta}; \quad Eu_{65}^{154} \rightarrow Gd_{64}^{154} + \overset{\nearrow}{\beta}.$$

$$Eu_{63}^{151} + n \rightarrow Eu_{63}^{152}; \qquad Eu_{63}^{153} + n \rightarrow Eu_{63}^{154},$$

$$Gd_{64}^{152} + n \rightarrow Eu_{63}^{152} + \overset{\nearrow}{p}; \quad Gd_{64}^{154} + n \rightarrow Eu_{63}^{154} + \overset{\nearrow}{p}.$$

Gadolinium.

$$Gd_{64}^{159} \rightarrow Tb_{65}^{159} + \overset{\nearrow}{\beta}.$$

$$Gd_{64}^{158} + n \rightarrow Gd_{64}^{159},$$

$$Tb_{65}^{159} + n \rightarrow Gd_{64}^{159} + \overset{\nearrow}{p}.$$

Dysprosium.

$$Dy_{66}^{165} \rightarrow Ho_{67}^{165} + \overset{\nearrow}{\beta}.$$

$$Dy_{66}^{164} + n \rightarrow Dy_{66}^{165},$$

$$Ho_{67}^{165} + n \rightarrow Dy_{66}^{165} + \overset{\nearrow}{p},$$

$$Er_{68}^{168} + n \rightarrow Dy_{66}^{165} + \overset{\nearrow}{\alpha}.$$

Holmium.

$$Ho_{67}^{166} \rightarrow Er_{68}^{166} + \overset{\nearrow}{\beta}.$$

$$Ho_{67}^{165} + n \rightarrow Ho_{67}^{166},$$

$$Er_{68}^{166} + n \rightarrow Ho_{67}^{166} + \overset{\nearrow}{p}.$$

Erbium.

$$Er_{68}^{169} \rightarrow Tu_{69}^{169} + \overset{\nearrow}{\beta}.$$

$$Er_{68}^{168} + n \rightarrow Er_{68}^{169},$$

$$Tu_{69}^{169} + n \rightarrow Er_{68}^{169} + \overset{\nearrow}{p},$$

$$Yb_{70}^{172} + n \rightarrow Er_{68}^{169} + \overset{\nearrow}{\alpha}.$$

Ytterbium.

$$Yt_{70}^{175} \rightarrow Lu_{71}^{175} + \overset{\nearrow}{\beta}.$$

$$Yt_{70}^{174} + n \rightarrow Yt_{70}^{175},$$

$$Lu_{71}^{175} + n \rightarrow Yt_{70}^{175} + \overset{\nearrow}{p},$$

$$Hf_{72}^{178} + n \rightarrow Yt_{70}^{175} + \overset{\nearrow}{\alpha}.$$

Lucetium.

$$Lu_{71}^{176} \rightarrow Hf_{72}^{176} + \overset{\nearrow}{\beta}.$$

$$Lu_{71}^{175} + n \rightarrow Lu_{71}^{176},$$

$$Hf_{72}^{176} + n \rightarrow Lu_{71}^{176} + \overset{\nearrow}{p}.$$

Hafnium.

$$Hf_{72}^{181} \rightarrow Ta_{73}^{181} + \overset{\nearrow}{\beta}.$$

$$Hf_{72}^{180} + n \rightarrow Hf_{72}^{181},$$

$$Ta_{73}^{181} + n \rightarrow Hf_{72}^{181} + \overset{\nearrow}{p},$$

$$W_{74}^{184} + n \rightarrow Hf_{72}^{181} + \overset{\nearrow}{\alpha}.$$

10. β-radioactive Isotopes of the Elements from Tantalum to Thallium.

Tantalum.

$$Ta_{73}^{182} \rightarrow W_{74}^{182} + \overset{\nearrow}{\beta}.$$

$$Ta_{73}^{181} + n \rightarrow Ta_{73}^{182},$$

$$W_{74}^{182} + n \rightarrow Ta_{73}^{182} + \overset{\nearrow}{p},$$

so we should anticipate the production of radioactive tantalum by bombarding tungsten with neutrons of high energy.

Tungsten.

$$W_{74}^{185} \rightarrow Re_{75}^{185} + \overset{\nearrow}{\beta}; \quad W_{74}^{187} \rightarrow Re_{75}^{187} + \overset{\nearrow}{\beta}.$$

$$W_{74}^{184} + n \rightarrow W_{74}^{185}; \qquad W_{74}^{186} + n \rightarrow W_{74}^{187},$$

$$Re_{75}^{185} + n \rightarrow W_{74}^{185} + \overset{\nearrow}{p}; \quad Re_{75}^{187} + n \rightarrow W_{74}^{187} + \overset{\nearrow}{p},$$

$$Os_{76}^{188} + n \rightarrow W_{74}^{185} + \overset{\nearrow}{\alpha}; \quad Os_{76}^{190} + n \rightarrow W_{74}^{187} + \overset{\nearrow}{\alpha},$$

and in view of the abundance of the isotopes concerned we suggest that all of these reactions could be produced with incident neutrons of the requisite energy.

Rhenium.

$$Re_{75}^{186} \rightarrow Os_{76}^{186} + \overset{\nearrow}{\beta}; \quad Re^{188} \rightarrow Os_{76}^{188} + \overset{\nearrow}{\beta}.$$

$$Re_{75}^{185} + n \rightarrow Re_{75}^{186}; \qquad Re_{75}^{187} + n \rightarrow Re_{75}^{188},$$

$$Os_{76}^{186} + n \rightarrow Re_{75}^{186} + \overset{\nearrow}{p}; \quad Os_{76}^{188} + n \rightarrow Re_{75}^{188} + \overset{\nearrow}{p}.$$

The osmium isotopes exist in small quantity, so the simple neutron capture process appears the more promising method of production.

Osmium.

$$Os_{76}^{191} \rightarrow Ir_{77}^{191} + \overset{\nearrow}{\beta}; \quad Os_{76}^{193} \rightarrow Ir_{77}^{193} + \overset{\nearrow}{\beta}.$$

$$Os_{76}^{190} + n \rightarrow Os_{76}^{191}; \qquad Os_{76}^{192} + n \rightarrow Os_{76}^{193},$$

$$Ir_{77}^{191} + n \rightarrow Os_{76}^{191} + \overset{\nearrow}{p}; \quad Ir_{77}^{193} + n \rightarrow Os_{76}^{193} + \overset{\nearrow}{p},$$

$$Pt_{78}^{194} + n \rightarrow Os_{76}^{191} + \overset{\nearrow}{\alpha}; \quad Pt_{78}^{196} + n \rightarrow Os_{76}^{193} + \overset{\nearrow}{\alpha}.$$

The isotopes of iridium, platinum, and gold have not yet been investigated, but, since the probable isotopes of these elements have been predicted *, we propose to discuss the possible radioactive isotopes on the hypothesis that missing isotopes are β-radioactive.

Iridium.

$$Ir_{77}^{192} \rightarrow Pt_{78}^{192} + \overset{\nearrow}{\beta}; \quad Ir_{77}^{194} \rightarrow Pt_{78}^{194} + \overset{\nearrow}{\beta}.$$

$$Ir_{77}^{191} + n \rightarrow Ir_{77}^{192}; \qquad Ir_{77}^{193} + n \rightarrow Ir_{77}^{194},$$

$$Pt_{78}^{192} + n \rightarrow Ir_{77}^{192} + \overset{\nearrow}{p}; \quad Pt_{78}^{194} + n \rightarrow Ir_{77}^{194} + \overset{\nearrow}{p},$$

$$Au_{79}^{197} + n \rightarrow Ir_{77}^{194} + \overset{\nearrow}{\alpha}.$$

Platinum.

$$Pt_{78}^{197} \rightarrow Au_{79}^{197} + \overset{\nearrow}{\beta}; \quad Pt_{78}^{199} \rightarrow Au_{79}^{199} + \overset{\nearrow}{\beta}.$$

$$Pt_{78}^{196} + n \rightarrow Pt_{78}^{197}; \qquad Pt_{78}^{198} + n \rightarrow Pt_{78}^{199},$$

$$Au_{79}^{197} + n \rightarrow Pt_{78}^{197} + \overset{\nearrow}{p}; \quad Au_{79}^{199} + n \rightarrow Pt_{78}^{199} + \overset{\nearrow}{p},$$

$$Hg_{80}^{200} + n \rightarrow Pt_{78}^{197} + \overset{\nearrow}{\alpha}; \quad Hg_{80}^{202} + n \rightarrow Pt_{78}^{199} + \overset{\nearrow}{\alpha}.$$

The last reaction should be realized experimentally, provided the energy of the bombarding neutrons is sufficiently great, since Hg^{200} and Hg^{202} are abundant.

* See Walke, Phil. Mag. xix. p. 33 (1935).

Gold.

$$Au_{79}^{198} \rightarrow Hg_{80}^{198} + \overset{\nearrow}{\beta}; \quad Au_{79}^{200} \rightarrow Hg_{80}^{200} + \overset{\nearrow}{\beta}.$$

$$Au_{79}^{197} + n \rightarrow Au_{79}^{198}; \qquad Au_{79}^{199} + n \rightarrow Au_{79}^{200},$$

$$Hg_{80}^{198} + n \rightarrow Au_{79}^{198} + \overset{\nearrow}{p}; \quad Hg_{80}^{200} + n \rightarrow Au_{79}^{200} + \overset{\nearrow}{p},$$

$$Tl_{81}^{203} + n \rightarrow Au_{79}^{200} + \overset{\nearrow}{\alpha}.$$

Mercury.

$$Hg_{80}^{205} \rightarrow Tl_{81}^{205} + \overset{\nearrow}{\beta}.$$

$$Hg_{80}^{204} + n \rightarrow Hg_{80}^{205},$$

$$Tl_{81}^{205} + n \rightarrow Hg_{80}^{205} + \overset{\nearrow}{p},$$

$$Pb_{82}^{208} + n \rightarrow Hg_{80}^{205} + \overset{\nearrow}{\alpha}.$$

Hence radioactive mercury should be produced when lead is bombarded with high-energy neutrons.

Thallium.

$$Tl_{81}^{204} \rightarrow Pb_{82}^{204} + \overset{\nearrow}{\beta}; \quad Tl_{81}^{206} \rightarrow Pb_{82}^{206} + \overset{\nearrow}{\beta}.$$

$$Tl_{81}^{203} + n \rightarrow Tl_{81}^{204}; \qquad Tl_{81}^{205} + n \rightarrow Tl_{81}^{206},$$

$$Pb_{82}^{204} + n \rightarrow Tl_{81}^{204} + \overset{\nearrow}{p}; \quad Pb_{82}^{206} + n \rightarrow Tl_{81}^{206} + \overset{\nearrow}{p},$$

$$Bi_{83}^{209} + n \rightarrow Tl_{81}^{206} + \overset{\nearrow}{\alpha},$$

Pb^{204} is scarce, but radioactive thallium should be formed when lead, or bismuth, is bombarded with high-speed neutrons. The reaction with bismuth is most probable, as the disintegration of Bi^{210} in the radium series, and the β-radioactivity of Tl^{206} in the same series, indicate that with the formation of Tl^{206} by neutron bombardment we are able to reproduce artificially the end-products of the natural radioactive series. The isotopes thus produced artificially should disintegrate in a manner similar to that of the corresponding natural radioactive isotopes.

11. Conclusion.

The phenomena which are likely to be observed experimentally when neutrons bombard elements—especially those of even atomic number—are in general complex, due to the formation of several β-radioactive isotopes from the various stable isotopes present in any one element. If the neutrons are of low energy, simple neutron capture results, whereas when high-energy neutrons are used disintegration generally occurs. It is probable that the excess energy is emitted in the form of γ-radiation. The definite experimental evidence of α-particle and proton emission from N^{14}, and the production of radioactive manganese from cobalt and iron, indicate that a radioactive isotope may be formed from different nuclei—the nuclei under neutron bombardment of different energies emitting different components. Thus we anticipate that experimental investigation of the relationship between induced radioactivity and energy of the bombarding neutrons will indicate missing radioactive isotopes formed by means of the nuclear disintegrations suggested in this paper.

12. Summary.

Missing isotopes of elements are regarded as being unstable, transmuting spontaneously with β-ray emission into stable isotopes of elements of which the atomic number is greater, by unity, than that of the radioactive one.

In some cases the radioactive isotope may give rise by β-ray disintegration to a second unstable nucleus, and a double transformation then occurs.

Reactions are indicated whereby these radioactive isotopes may be produced by bombarding elements with neutrons. The types of reaction are simple neutron capture, and disintegration with proton, or α-particle, emission.

Some of the predicted reactions have already been confirmed experimentally by various workers, and the decay periods of the induced radioactivity determined.

University College, Exeter.
September 3rd, 1934.

LIII. *The Quantum Statistical Theory of Spontaneous Fluctuation.* *By* M. GHOSH, *M.Sc., A.Inst.P.**

THE fluctuations of different quantities, such as density, pressure, energy, etc., have long been derived by different workers [1] with the help of classical statistics. In 1923 Kar [2] derived some important classical relations between different partial fluctuations. With the help of these, and from two partial fluctuations obtained independently by statistical methods, he obtained the expressions for all other fluctuations known.

Einstein [3] was the first to apply the new quantum statistics and derive the formula for the energy fluctuation of radiation per cell. He, however, used the classical expression for dispersion. Recently Fürth [4] has studied the problem anew from the point of view of quantum statistics, and obtained the fluctuations for only the non-degenerate case; but his derivations are more or less classical, since, as he himself has shown, his results are all obtainable directly from the classical relations of dispersion.

In this paper we propose to generalize the partial relations of Kar both for the non-degenerate and the degenerate case, and to calculate two partial fluctuations, viz., the energy fluctuation at constant volume and the density fluctuation at constant temperature, with the help of quantum statistics. From these two partial fluctuations, and with the help of the above generalized partial relations, we shall be able to derive all the fluctuations yet known.

(a) *Energy Fluctuation.*

It is well known according to the new statistics that the total number [5] of s type molecules is

$$N_s = A_s \Big/ \left(e^{\frac{\psi + u_s}{KT}} \mp 1\right). \quad . \quad . \quad . \quad (1)$$

So

$$N = \Sigma N_s = \frac{2\pi V}{h^3} (2m)^{3/2} \int_0^\infty \frac{u_s^{1/2}\, du_s}{e^{\frac{\psi + u_s}{KT}} \mp 1}$$

$$= \frac{2\pi V}{h^3} (2m\,KT)^{3/2} \Gamma\left(\frac{3}{2}\right) F_{1/2}\left(\frac{\psi}{KT}\right), \quad . \quad . \quad (2)$$

* Communicated by Prof. K. C. Kar, D.Sc.

where the upper sign, which is −ve, is for Bose statistics, and the lower sign, which is +ve, is for Fermi statistics.

The average energy per molecule is

$$u = \frac{\sum_s N_s u_s}{\sum_s N_s} = \int_0^\infty \frac{u_s^{3/2}\,du_s}{e^{\frac{-\psi+u_s}{KT}} \mp 1} \Big/ \int_0^\infty \frac{u_s^{1/2}\,du_s}{e^{\frac{-\psi+u_s}{KT}} \mp 1}$$

$$= \frac{3\,KTF_{3/2}(\psi/KT)}{2\,KTF_{1/2}(\psi/KT)} \quad . \quad . \quad . \quad (3)$$

Similarly

$$u^2 = \frac{\sum_s N_s u_s^2}{\sum_s N_s} = \frac{15}{4}(KT)^2 \frac{F_{5/2}(\psi/KT)}{F_{1/2}(\psi/KT)}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $F_r(\psi/KT)$, the Sommerfeld's integral, is given by

$$F_r(\psi/KT) = \frac{1}{\Gamma(r+1)} \int_0^\infty \frac{x^r\,dx}{e^{-\frac{\psi}{KT}+x} \mp 1}$$

$$= e^{\psi/KT}\left(1 \pm \frac{e^{\frac{\psi}{KT}}}{2^{r+1}} + \frac{e^{\frac{2\psi}{KT}}}{3^{r+1}} \pm \dots\right)$$

non-degenerate . . . (5)

$$= \frac{(\psi/KT)^{r+1}}{\Gamma(r+2)}\left[1 + 2\left\{\frac{r(r+1)}{(\psi/KT)^2} C_2 + \frac{(r-2)(r-1)r(r+1)}{(\psi/KT)^4} C_4 \dots\right\}\right]$$

degenerate (Fermi), . . . (6)

where for the non-degenerate state

$$e^{\frac{\psi}{KT}} = \frac{N}{V}\frac{h^3}{(2\pi m\,KT)^{3/2}}\left[1 \mp \frac{1}{2^{3/2}} \cdot \frac{N}{V} \cdot \frac{h^3}{(2\pi m\,KT)^{3/2}} - \dots\right], \quad (7)$$

and for the degenerate state (Fermi)

$$\frac{\psi}{KT} = \left(\frac{3N}{4\pi V}\right)^{2/3} \frac{h^2}{2m\,KT}\left[1 - C_2\left(\frac{4\pi V}{3N}\right)^{4/3} \cdot \frac{(2m\,KT)^2}{h^4} \dots\right],$$

. . . (8)

where $$C_2 = \frac{\pi^2}{12}.$$

Now, the dispersion of energy per molecule, as usually defined, is

$$\overline{u^2} - (\bar{u})^2; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

so the dispersion for N molecules is

$$N(\overline{u^2} - |\bar{u}|^2), \quad . \quad . \quad . \quad . \quad . \quad (10)$$

which is easily seen to be the dispersion of energy for the γ-space of 6N dimensions [6].

Accordingly, the fluctuation of energy $(\overline{\delta_E^2})_V$ for N molecules at constant volume is given by

$$(\overline{\delta_E^2})_V = \frac{N(\overline{u^2} - |\bar{u}|^2)}{(N\bar{u})^2} = \frac{1}{N} \cdot \frac{\overline{u^2} - |\bar{u}|^2}{|\bar{u}|^2}. \quad . \quad . \quad (11)$$

Non-degenerate Case.

From eqs. (3) and (4) we get, by putting the values of $F_{5/2}\left(\frac{\psi}{KT}\right)$, $F_{3/2}\left(\frac{\psi}{KT}\right)$, and $F_{1/2}\left(\frac{\psi}{KT}\right)$ from (5) and (7),

$$u = \frac{3}{2}KT\left(1 \mp \frac{1}{2}\frac{e^{\frac{\psi}{KT}}}{2^{3/2}}\right) = \frac{3}{2}KT\left(1 \mp \frac{1}{2}y\right), \quad . \quad . \quad (12a)$$

$$\overline{u^2} = \frac{15}{4}(KT)^2\left(1 \mp \frac{3}{4}\frac{e^{\frac{\psi}{KT}}}{2^{3/2}}\right) = \frac{15}{4}(KT)^2\left(1 \mp \frac{3}{4}y\right), \quad (12b)$$

where

$$y = \frac{N}{V} \cdot \frac{h^3}{(4\pi m KT)^{3/2}}; \quad . \quad . \quad . \quad . \quad (13)$$

with the help of (12) we have for the fluctuation of energy at constant volume (*cf.* eq. (11))

$$(\overline{\delta_E^2})_V = \frac{2}{3N}\left(1 \pm \frac{5}{8}y\right). \quad . \quad . \quad . \quad . \quad (14)$$

The positive sign within the bracket is for Bose statistics, and the negative sign for Fermi statistics.

Degenerate Case.

The degenerate values of $\bar{u}$ and u^2 are obtained by putting the corresponding values of the functions from (6) and (8), whence we get

$$u = \frac{3}{5}\mathrm{KTZ}\left(1+\frac{5C_2}{Z^2}\right), \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

$$\bar{u^2} = \frac{3}{7}(\mathrm{KTZ})^2\left(1+\frac{14C_2}{Z^2}\right), \quad . \quad . \quad . \quad (16)$$

where $$Z = \left(\frac{3N}{4\pi V}\right)^{2/3}\frac{h^2}{2m\,KT} \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

From eqs. (15) and (16), eq. (11) becomes

$$(\overline{\delta_E^2})_V = \frac{4}{21N}\left(1+\frac{25C_2}{Z^2}\right), \quad . \quad . \quad . \quad (18)$$

which is the energy fluctuation for the degenerate state.

(b) *Density Fluctuation at Constant Temperature.*

Let us consider an element of volume of the fluid containing N molecules. The density ρ and consequently the specific volume $V\left(=\frac{1}{\rho}\right)$ of the fluid, instead of remaining constant, will fluctuate about the mean values ρ_0 and $V_0\left(=\frac{1}{\rho_0}\right)$. The work χ, done isothermally in bringing about a small change in the elementary volume, with the consequent change of pressure from the equilibrium value to any value p, is [1] per molecule

$$\chi = -\int_{V_0}^{V}(p-p_0)\,dV = -\left[\left(\frac{\partial p}{\partial V}\right)_0\frac{(V-V_0)^2}{2!} + \left(\frac{\partial^2 p}{\partial V^2}\right)_0\frac{(V-V_0)^3}{3!} + + \right] \text{ (by Maclaurin's theorem)}$$

$$= -\left[\frac{V_0^2}{2}\left(\frac{\partial p}{\partial V}\right)_0\sigma^2 + \frac{V_0^3}{6}\left(\frac{\partial^2 p}{\partial V^2}\right)_0\sigma^3 + + \right], \quad . \quad . \quad (19)$$

where σ represents the condensation and is given by

$$\sigma = \frac{V-V_0}{V_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

The above work may be taken as the potential energy per molecule for the given volume.

Now we know that

$$p\mathrm{V}=\mathrm{KT}\frac{\mathrm{F}_{3/2}\left(\frac{\psi}{\mathrm{KT}}\right)}{\mathrm{F}_{1/2}\left(\frac{\psi}{\mathrm{KT}}\right)}=\frac{2}{3}u\,; \quad . \quad . \quad . \quad (21)$$

therefore on differentiating

$$\frac{\partial p}{\partial \mathrm{V}}=\frac{2}{3\mathrm{V}^2}\left[\mathrm{V}\frac{\partial u}{\partial \mathrm{V}}-u\right]. \quad . \quad . \quad . \quad . \quad (22)$$

From (19), neglecting powers of σ higher than the second, we have

$$-\frac{\chi}{\mathrm{KT}}=\frac{1}{3\mathrm{KT}}\left[\mathrm{V}\frac{\partial u}{\partial \mathrm{V}}-u\right]\sigma^2. \quad . \quad . \quad . \quad (23)$$

On taking into account the above potential energy [9] we get from (1)

$$\mathrm{N}_s=\mathrm{A}_s\Big/\left(e^{\frac{-\psi+\chi+u_s}{\mathrm{KT}}}\mp 1\right)=\frac{2\pi \mathrm{V}_0}{h^3}(2m)^{3/2}\cdot\frac{u_s^{1/2}\,du_s}{e^{\frac{-\psi+\chi+u_s}{\mathrm{KT}}}\mp 1}\cdot d\sigma,$$

since $d\sigma=\dfrac{d\mathrm{V}}{\mathrm{V}_0}$ from (20).

So

$$\mathrm{N}=\sum_s \mathrm{N}_s=\frac{2\pi \mathrm{V}_0}{h^3}(2m\,\mathrm{KT})^{3/2}\Gamma\left(\frac{3}{2}\right)\int_0^\infty \mathrm{F}_{1/2}\left(\frac{\psi-\chi}{\mathrm{KT}}\right)d\sigma. \quad . \quad (24)$$

Accordingly the density fluctuation per molecule is given by

$$\overline{\sigma^2}=\int_0^\infty \mathrm{F}_{1/2}\left(\frac{\psi-\chi}{\mathrm{KT}}\right)\sigma^2\,d\sigma\Big/\int_0^\infty \mathrm{F}_{1/2}\left(\frac{\psi-\chi}{\mathrm{KT}}\right)d\sigma.$$

So for N molecules the density fluctuation is given by (as in eq. (11)).

$$(\overline{\delta_\rho^2})_{\mathrm{T}}=\frac{1}{\mathrm{N}}\cdot\frac{\int_0^\infty \mathrm{F}_{1/2}\left(\frac{\psi-\chi}{\mathrm{KT}}\right)\sigma^2\,d\sigma}{\int_0^\infty \mathrm{F}_{1/2}\left(\frac{\psi-\chi}{\mathrm{KT}}\right)d\sigma}. \quad . \quad . \quad (25)$$

Non-degenerate Case.

Substituting the values of $\frac{\partial u}{\partial V}$ and u from (12a) in (23) we get

$$\frac{\chi}{KT}=\beta_1\sigma^2,$$

where $$\beta_1=\tfrac{1}{2}(1\mp y). \quad . \quad . \quad . \quad . \quad (26)$$

Now we have from (5) for the non-degenerate state, as

$$\frac{\chi}{KT}=\beta_1\sigma^2,$$

$$F_{1/}\left(\frac{\psi-\chi}{KT}\right)=F_{1/2}\left(\frac{\psi}{KT}-\beta_1\sigma^2\right)$$

$$=e^{\left(\frac{\psi}{KT}-\beta_1\sigma^2\right)}\left\{1\pm\frac{e^{\left(\frac{\psi}{KT}-\beta_1\sigma^2\right)}}{2^{3/2}}\right.$$

$$\left.+\frac{e^{2\left(\frac{\psi}{KT}-\beta_1\sigma^2\right)}}{3^{3/2}}\pm\ldots\right\}. \quad (27)$$

So

$$\int_0^\infty F_{1/2}\left(\frac{\psi}{KT}-\beta_1\sigma^2\right)\sigma^2\,d\sigma=\frac{F_2\left(\frac{\psi}{KT}\right)}{\beta_1^{3/2}}\int_0^\infty e^{-\xi^2}\xi^2\,d\xi,$$

and

$$\int_0^\infty F_{1/2}\left(\frac{\psi}{KT}-\beta_1\sigma^2\right)d\sigma=\frac{F_1\left(\frac{\psi}{KT}\right)}{\beta_1^{1/2}}\int_0^\infty e^{-\xi^2}\,d\xi.$$

With the help of (27) eq. (25) becomes

$$(\bar{\delta}_n^2)_T=\frac{1}{\beta_1 N}\frac{F_2\left(\frac{\psi}{KT}\right)}{F_1\left(\frac{\psi}{KT}\right)}\cdot\frac{\int_0^\infty e^{-\xi^2}\xi^2\,d\xi}{\int_0^\infty e^{-\xi^2}\,d\xi}=\frac{1}{2N\beta_1}\frac{F_2\left(\frac{\psi}{KT}\right)}{F_1\left(\frac{\psi}{KT}\right)}. \quad (28)$$

From eqs. (5), (13), and (26)

$$(\bar{\delta}_n^2)_T=\frac{1}{N}(1\pm\cdot647y). \quad . \quad . \quad . \quad . \quad (29)$$

It should be noted that Fürth's value for the above, namely, $\frac{1}{N}(1\pm y)$, can very easily be obtained from (28), using the quantum value from (26) and the classical value unity for the ratio $F_2\left(\frac{\psi}{KT}\right)\Big/F_1\left(\frac{\psi}{KT}\right)$.

Degenerate Case.

In this case the value of $\frac{\chi}{KT}$ is obtained by substituting the value of $\bar{u}$ in eq. (22) from (15). This gives

$$\frac{\chi}{KT}=\beta_2\sigma^2,$$

where
$$\beta_2=\frac{Z}{3}\left(1+\frac{C_2}{Z^2}\right). \quad . \quad . \quad . \quad . \quad . \quad (30)$$

The value of $F_{1/2}\left(\frac{\psi}{KT}-\beta_2\sigma^2\right)$ is obtained from (6), and we have

$$F_{1/2}\left(\frac{\psi}{KT}-\beta_2\sigma^2\right)=\frac{1}{\Gamma(\frac{5}{2})}\cdot\left(\frac{\psi}{KT}\right)^{3/2}\cdot\left(1-\frac{\beta_2 KT}{\psi}\sigma^2\right)^{3/2}$$
$$\times\left\{1+\frac{3C_2}{2}\left(\frac{\psi}{KT}\right)^{-2}\left(1-\frac{\beta_2 KT}{\psi}\sigma^2\right)^{-2}\right\}. \quad . \quad (31)$$

Thus from eq. (31), eq. (25) becomes

$$(\overline{\delta_\rho^2})_T=\frac{\frac{1}{N}\displaystyle\int_0^{\sqrt{\frac{\psi}{\beta_2 KT}}}\left(1-\frac{\beta_2 KT}{\psi}\sigma^2\right)^{3/2}\left\{1+\frac{3C_2}{2}\left(\frac{\psi}{KT}\right)^{-2}\times\left(1-\frac{\beta_2 KT}{\psi}\sigma^2\right)^{-2}\right\}\sigma^2 d\sigma}{\displaystyle\int_0^{\sqrt{\frac{\psi}{\beta_2 KT}}}\left(1-\frac{\beta_2 KT}{\psi}\sigma^2\right)^{3/2}\left\{1+\frac{3C_2}{2}\left(\frac{\psi}{KT}\right)^{-2}\times\left(1-\frac{\beta KT}{\psi}\sigma^2\right)^{-2}\right\}d\sigma}$$
$$. \quad . \quad . \quad (32)$$

Here the upper limit of the integration is taken, $\sqrt{\frac{\psi}{\beta_2 KT}}$, instead of infinity, since from the condition of

degeneracy, $\frac{\chi}{KT}$, *i. e.*, $\beta_2\sigma^2$ cannot be greater than $\frac{\psi}{KT}$, so $\sigma^2 \not> \frac{\psi}{\beta_2 KT}$.

Now putting $\frac{\beta_2 KT\sigma^2}{\psi} = \sin\xi$ eq. (32) becomes

$$(\overline{\delta_\rho^2})_T = \frac{\psi}{\beta_2 NKT} \frac{\int_0^{\frac{\pi}{2}} \sin^2\xi\cos^4\xi\, d\xi + \frac{3}{2}C_2\left(\frac{\psi}{KT}\right)^{-2}\int_0^{\frac{\pi}{2}} \sin^2\xi\, d\xi}{\int_0^{\frac{\pi}{2}} \cos^4\xi\, d\xi + \frac{3}{2}C_2\left(\frac{\psi}{KT}\right)^{-2}\int_0^{\frac{\pi}{2}} d\xi} \quad . \quad . \quad . \quad (33)$$

On putting the values of β_2 and $\frac{\psi}{KT}$ from eqs. (30), (8), and (17), we get from (33), after integration,

$$(\overline{\delta_\rho^2})_T = \frac{1}{2N}\left(1 + \frac{6C_2}{Z^2}\right). \quad . \quad . \quad . \quad . \quad . \quad (34)$$

(c) *Relation between different kinds of Fluctuations.*

After evaluating $(\overline{\delta_\kappa^2})_V$ and $(\delta_\rho^2)_T$ from the dispersion theory we shall next proceed to find the other fluctuations known from the fundamental relations to be deduced just now.

Non-degenerate Case.

From eq. (12*a*), putting the values of $\bar{u}$ in eq. (21) we get

$$PV = NKT(1 \mp y) = \tfrac{2}{3}\overline{E} \quad (\text{as } \overline{E} = N\bar{u}), \quad . \quad (35a)$$

after logarithmic differentiation we have

$$\frac{\Delta P}{P} + \frac{\Delta V}{V} = \frac{\Delta T}{T}\left(1 \pm \tfrac{3}{4}y\right) \pm \frac{y}{2}\left(1 \mp \frac{y}{2}\right)\frac{\Delta V}{V} = \frac{\Delta\overline{E}}{\overline{E}}; \quad (35b)$$

whence we get

$$\frac{\Delta P}{P} + \frac{\Delta V}{V}\left(1 \mp \frac{y}{2}\right) = \frac{\Delta T}{T}\left(1 \pm \tfrac{3}{4}y\right) \quad . \quad (36a)$$

and

$$\frac{\Delta\overline{E}}{\overline{E}} = \frac{\Delta T}{T}\left(1 \pm \tfrac{3}{4}y\right) \pm \frac{\Delta V}{V}\frac{y}{2}. \quad . \quad . \quad (36b)$$

In the case where T is constant $\Delta T=0$; so from (36a) we get, after squaring and taking mean,

$$(\delta_V^2)_T(1\mp y)=(\bar{\delta}_P^2)_T. \quad . \quad . \quad . \quad . \quad . \quad (37)$$

In the case where P is constant $\Delta P=0$, and so from (36a) we have for the corresponding relation

$$(\delta_V^2)_P(1\mp\tfrac{5}{2}y)=(\bar{\delta}_T^2)_P \quad . \quad . \quad . \quad . \quad . \quad (38)$$

Similarly where V is constant we have

$$(\bar{\delta}_P^2)_V(1\mp\tfrac{3}{2}y)=(\bar{\delta}_T^2)_V, \quad . \quad . \quad . \quad . \quad (39)$$

and from (35b) we get

$$(\bar{\delta}_P^2)_V=(\delta_E^2)_V. \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

Again, from (36b) we get in the same way as above

$$(\bar{\delta}_E^2)_V=(\delta_T^2)_V(1\pm\tfrac{3}{2}y), \quad . \quad . \quad . \quad . \quad (41)$$

and

$$(\bar{\delta}_E^2)_T=\frac{y^2}{4}.(\delta_V^2)_T. \quad . \quad . \quad . \quad . \quad . \quad (42)$$

Since $(\delta_V^2)_T$ is of the order $\frac{1}{N}$ and y is small, it follows from (42) that the isothermal energy fluctuation must be negligibly small. It is otherwise evident from the fact that energy mainly depends upon temperature.

Previously we have got (*cf.* eqs. (29) and (14))

$$(\bar{\delta}_V^2)_T=\frac{1}{N}(1\pm 0{\cdot}647y) \quad . \quad . \quad . \quad . \quad (43)$$

and

$$(\bar{\delta}_E^2)_T=\frac{2}{3N}\left(1\pm\frac{5}{8}y\right). \quad . \quad . \quad . \quad . \quad (44)$$

From (41), on substituting the value of $(\bar{\delta}_E^2)_V$ from (44),

$$(\bar{\delta}_T^2)_V=\frac{2}{3N}(1\mp 0{\cdot}875y) \quad . \quad . \quad . \quad . \quad (45)$$

Again we have for total fluctuation of pressure

$$(\bar{\delta}_P^2)=(\bar{\delta}_P^2)_V+(\bar{\delta}_P^2)_T$$

$$=(\delta_E^2)_V+(\delta_V^2)_T(1\mp y) \text{ from eqs. (31) and (40)}$$

$$=\frac{5}{3N}(1\pm 0{\cdot}039y). \quad . \quad . \quad . \quad . \quad (46)$$

Degenerate Case.

On putting in eq. (21) the degenerate value of $\bar{u}$ from (15) we have

$$PV = \frac{2}{5}NKTZ\left(1+\frac{5C_2}{Z^2}\right) \quad . \quad . \quad . \quad . \quad (47)$$

By logarithmic differentiation of (47) we get

$$\frac{\Delta P}{\bar{P}} + \frac{5}{3}\left(1-\frac{4C_2}{Z^2}\right)\frac{\Delta V}{V} = \frac{10C_2}{Z^2}\cdot\frac{\Delta T}{\bar{T}}, \quad . \quad . \quad (48)$$

whence we have the following relations

$$\frac{25}{9}\left(1-\frac{8C_2}{Z^2}\right)(\overline{\delta_V^2})_T = (\delta_P^2)_T, \quad . \quad . \quad . \quad . \quad (49)$$

$$\frac{25}{9}\left(1-\frac{8C_2}{Z^2}\right)(\overline{\delta_V^2})_P = \left(\frac{10C_2}{Z^2}\right)^2(\delta_T^2)_P, \quad . \quad . \quad . \quad (50)$$

$$(\overline{\delta_E^2})_V = (\overline{\delta_r^2}) = \frac{10C_2}{Z^2}(\overline{\delta_T^2})_V, \quad . \quad . \quad . \quad . \quad (51)$$

but we have already, in (34) and (29),

$$(\overline{\delta_V^2})_T = \frac{1}{2\bar{N}}\left(1+\frac{6C_2}{Z^2}\right), \quad . \quad . \quad . \quad . \quad (52a)$$

$$(\overline{\delta_E^2})_V = \frac{4}{21\bar{N}}\left(1+\frac{25C_2}{Z^2}\right). \quad . \quad . \quad . \quad (52b)$$

As before we have

$$\begin{aligned}(\overline{\delta_P^2}) &= (\delta_P^2)_V + (\delta_P^2)_T \\ &= (\overline{\delta_E^2})_V + \frac{25}{9}\left(1-\frac{8C_2}{Z^2}\right)(\delta_V^2)_T \\ &= \frac{1{\cdot}58}{\bar{N}}\left(1+1{\cdot}130\,\frac{C_2}{Z^2}\right), \quad . \quad . \quad . \quad . \quad (53)\end{aligned}$$

and

$$\begin{aligned}(\overline{\delta_T^2})_V &= \left(\frac{Z^2}{10C_2}\right)^2(\overline{\delta_E^2})_V \\ &= \frac{4}{21\bar{N}}\left(\frac{Z^2}{10C_2}\right)^2\left(1+\frac{25C_2}{Z^2}\right). \quad . \quad . \quad (54)\end{aligned}$$

Thus we see that $(\overline{\delta_T^2})_V$ is very small, since Z is small.

(d) *Fluctuation within the Cell.*

As in Kar-Mazumdar [5] statistics, let $n_0^s, n_1^s, n_2^s, \ldots n_\lambda^s$ etc. be the number of s type cells containing zero, one, two, etc. quanta; then

$$\left.\begin{aligned} n_0^s &= A_s e^{\frac{\psi_s}{KT}}, \\ n_1^s &= A_s e^{\frac{\psi_s}{KT}} . e^{\frac{\psi - u_s}{KT}}, \\ n_2^s &= A_s e^{\frac{\psi_s}{KT}} . e^{\frac{2(\psi - u_s)}{KT}}, \\ &\cdots\cdots \\ &\cdots\cdots \\ n_s^\lambda &= A_s e^{\frac{\psi_s}{KT}} . e^{\frac{\lambda(\psi - u_s)}{KT}}, \end{aligned}\right\} \quad \ldots\ldots \quad (55)$$

where ψ_s is the free energy per "s" type cell and ψ the free energy per molecule; and as the total number of "s" type cell is given by

$$A_s = \sum_0^\infty n_\lambda^s \quad \text{(Bose)} \quad \ldots \quad (55a)$$

$$= \sum_0^1 n_\lambda^s \quad \text{(Fermi)}, \quad \ldots \quad (55b)$$

it follows immediately from (55) and (55a, b) that

$$e^{\pm \frac{\psi s}{KT}} = 1 \mp e^{\frac{\psi - u_s}{KT}} \quad \ldots\ldots \quad (56)$$

So the average number of molecules per cell is

$$\bar{N}_s = \frac{\sum_\lambda \lambda n_\lambda^s}{\sum_\lambda n_\lambda^s} = \frac{\sum_\lambda A_s \lambda e^{\frac{\psi_s}{KT}} . e^{\frac{\lambda(\psi - u_s)}{KT}}}{A_s}$$

$$= 1 \Big/ \left(e^{\frac{\psi - u_s}{KT}} \mp 1\right), \quad \ldots\ldots \quad (57)$$

where the summation extends from zero to infinity for the Bose statistics, and from zero to one for the Fermi statistics.

The square mean of the number of molecules per cell is

$$\left.\begin{aligned}\overline{N_s^2} &= \frac{\Sigma_\lambda \lambda^2 n_\lambda{}^s}{\Sigma_\lambda n_\lambda{}^s} \\ &= \left(1+e^{\frac{\psi-u_s}{KT}}\right) e^{\frac{\psi-u_s}{KT}} \Big/ \left(1-e^{\frac{\psi-u_s}{KT}}\right)^2 \quad \text{(Bose)} \\ &= e^{\frac{\psi-u_s}{KT}} \Big/ \left(1+e^{\frac{\psi-u_s}{KT}}\right). \quad \text{(Fermi)}\end{aligned}\right\} \quad (58)$$

The dispersion of the number per cell is

$$\overline{N_s^2} - |\overline{N}_s|^2 = e^{\frac{\psi-u_s}{KT}} \Big/ \left(1-e^{\frac{\psi-u_s}{KT}}\right)^2 \text{ (from (57) and (58))}, \quad (59)$$

and so the fluctuation is

$$(\delta^2_{N_s}) = \frac{\overline{N_s^2} - |\overline{N}^s|^2}{|\overline{N}_s|^2} = e^{-\frac{\psi-u_s}{KT}} = \frac{1}{\overline{N}_s} \pm 1. \quad . \quad . \quad (60)$$

This is the same as given by Schrödinger [8] and also by Fürth [4]. It is nothing but the fluctuation of the number per "*s*" type cell.

Let us now consider the total *s*-type fluctuation. We have for the total dispersion

$$\Delta_s = A_s(\overline{N_s^2} - |\overline{N}_s|^2) ; \quad . \quad . \quad . \quad . \quad . \quad (61)$$

so that the fluctuation is $\frac{\Delta_s}{(A_s\overline{N}_s)^2}$, which by eq. (59) becomes

$$\frac{\Delta_s}{(A_s\overline{N}_s)^2} = \frac{1}{N_s} \pm \frac{1}{A_s}, \quad . \quad . \quad . \quad . \quad . \quad (62)$$

since $$A_s\overline{N}_s = N_s.$$

In the case of radiation the energy fluctuation (per cell or per "*s*" type cell) is obviously equal to the number fluctuation as given by eq. (60) and (62). We may note that the eq. (62) was first obtained by Einstein as energy fluctuation of quanta.

(e) *The Classical and Quantum Fluctuation.*

From definition, the expression for the energy fluctuation of N molecules is $(E^2 - |E|^2)/|E|^2$, which, as shown before, is equivalent to $(\overline{u}^2 - |u|^2)/N|u|^2$ (*cf.* eq. (11)),

where E is the energy of the N molecules and u the energy per molecule. In the case of classical statistics the above expression is reducible to

$$\frac{\Theta^2}{N|\bar{u}|^2}\cdot\frac{\partial\bar{u}}{\partial\Theta}, \quad \ldots\ldots \quad (63)$$

where $\Theta=KT$. But it is not so in the new statistics, as will be shown below.

When $e^{\frac{\psi-u}{\Theta}}\ll 1$, eq. (3) may be written as

$$u=\int_0^\infty g_s u_s e^{\frac{\psi-u_s}{\Theta}}d\tau \int_0^\infty g_s e^{\frac{\psi-u_s}{\Theta}}d\tau, \quad \ldots \quad (64)$$

where $$g_s=\left(1\mp e^{\frac{\psi-u_s}{\Theta}}\right)^{-1}=1\pm e^{\frac{\psi-u_s}{\Theta}}+\ldots, \quad \ldots \quad (65)$$

and $$d\tau=2\pi V(2m)^{3/2}u_s^{1/2}du_s. \quad \ldots\ldots \quad (66)$$

On differentiating with respect to Θ we have from (64)

$$\left.\begin{aligned}\frac{\partial\bar{u}}{\partial\Theta}=\frac{1}{\Theta^2}&\left[\frac{\int_0^\infty u_s^2 g_s e^{-\frac{u_s}{\Theta}}d\tau}{\int_0^\infty g_s e^{-\frac{u_s}{\Theta}}d\tau}-\left\{\frac{\int_0^\infty u_s g_s e^{-\frac{u_s}{\Theta}}d\tau}{\int_0^\infty g_s e^{-\frac{u_s}{\Theta}}d\tau}\right\}^2\right]\\&+\frac{\int_0^\infty u_s\frac{\partial g_s}{\partial\Theta}e^{-\frac{u_s}{\Theta}}d\tau}{\int_0^\infty g_s e^{-\frac{u_s}{\Theta}}d\tau}-\frac{\int_0^\infty\frac{\partial g_s}{\partial\Theta}e^{-\frac{u_s}{\Theta}}d\tau}{\int_0^\infty g_s e^{-\frac{u_s}{\Theta}}d\tau}\\&\times\frac{\int_0^\infty\frac{\partial g_s}{\partial\Theta}\cdot e^{-\frac{u_s}{\Theta}}d\tau}{\int_0^\infty g_s e^{-\frac{u_s}{\Theta}}d\tau},\\=\frac{\overline{u^2}-|\bar{u}|^2}{\Theta^2}&-\left\{\int_0^\infty u_s\frac{\partial g_s}{\partial\Theta}e^{-\frac{u_s}{\Theta}}d\tau\right.\\&\left.-\bar{u}\int_0^\infty\frac{\partial g_s}{\partial\Theta}e^{-\frac{u_s}{\Theta}}d\tau\right\}\Big/\int_0^\infty g_s e^{-\frac{u_s}{\Theta}}d\tau,\end{aligned}\right\} \quad (67)$$

from the usual definition of $\bar{u}$ and $\overline{u^2}$.

Now, putting in (65) the value of $e^{-\frac{\psi}{\Theta}}$ from (6), we have

$$\frac{\partial g_s}{\partial \Theta} = \pm \frac{2^{3/2}}{\Theta^{\frac{1}{2}}} y \left\{ (1 \mp y) u_s e^{-\frac{u_s}{\Theta}} - \frac{3}{2} \Theta (1 \mp 2y) e^{-\frac{u_s}{\Theta}} \right\}.$$

Putting this value of $\frac{\partial g_s}{\partial \Theta}$, we get, after integration,

$$\left.\begin{aligned} \int_0^\infty \frac{\partial g_s}{\partial \Theta} u_s e^{-\frac{u_s}{\Theta}} d\tau &= \mp 2\pi \mathrm{V} (2m\Theta)^{3/2} \Gamma\left(\frac{5}{2}\right) \cdot \frac{1}{8} y (1 \mp 7y), \\ \int_0^\infty \frac{\partial g_s}{\partial \Theta} e^{-\frac{u_s}{\Theta}} d\tau &= \mp \frac{2\pi \mathrm{V}}{\Theta} (2m\Theta)^{3/2} \Gamma\left(\frac{5}{2}\right) \cdot \frac{1}{2} y (1 \mp 3y), \\ \text{and} \\ \int_0^\infty g_s e^{-\frac{u_s}{\Theta}} d\tau &= 2\pi \mathrm{V} (2m\Theta)^{3/2} \Gamma\left(\frac{5}{2}\right) \cdot \frac{2}{3} (1 \pm y). \end{aligned}\right\} \quad (68)$$

So with the help of (68), (67) can be written as

$$\overline{u^2} - |\bar{u}|^2 = \Theta^2 \frac{\partial u}{\partial \Theta} \mp \frac{3}{2} \Theta^2 \cdot \frac{5}{8} y. \quad . \quad . \quad . \quad (69)$$

Hence the fluctuation becomes

$$\frac{\overline{u^2} - |\bar{u}|^2}{\mathrm{N}|\bar{u}|^2} = \frac{\Theta^2}{\mathrm{N}|\bar{u}|^2} \cdot \frac{\partial u}{\partial \Theta} \mp \frac{3}{2} \frac{\Theta^2}{\mathrm{N}|\bar{u}|^2} \cdot \frac{5}{8} y. \quad . \quad . \quad (70)$$

In the case of classical distribution the second term on the right-hand side of eq. (70) is evidently zero. Putting the quantum value of $\bar{u}$ from eq. ($12a$) only in the first term of the right-hand side we get $\frac{2}{3\mathrm{N}}\left(1 \pm \frac{5}{4} y\right)$, which is Fürth's value of energy fluctuation. The corrected value will be obtained when the second term is also taken into account.

I express my sincere thanks to Prof. K. C. Kar, D.Sc., for his continuous encouragement and advice in the course of this work.

References.

(1) Smoluchwoski Boltzmann, 'Festschrift,' p. 626 (1904); Hauer, *Ann. der Phys.* xlvii. p. 365 (1915); Laue, *Phys. Zeit.* xviii. p. 542 (1917); Fürth, *Phys. Zeit.* xx. p. 350 (1919): also Fürth's 'Schwankungserscheinungen in der Physik.'

(2) Kar, Phys. Rev. xxi. p. 672 (1923); *Phys. Zeit.* xxiv. p. 429 (1923); xxv. p. 397 (1924).

(3) Einstein, *Preuss. Akad. d. Wiss.* p. 261 (1924); p. 3 (1925); Lorentz, 'Les théories statistiques en thermodynamique,' p. 114.
(4) Fürth, *Zeit. f. Phys.* xlviii. p. 325 (1928).
(5) Kar and Mazumdar, *Zeit. f. Phys.* lv. p. 546 (1929).
(6) Uhlenbeck and Gropper, Phys. Rev. xli. p. 80 (1932).
(7) M. Ghosh, 'Current Science,' p. 377 (June 1933).
(8) Schrödinger, *Phys. Zeit.* xxvii. p. 95 (1926).
(9) Pauli, *Zeit. f. Phys.* xli. p. 97 (1927). *Vide* in the case of paramagnetism.

Physical Research Laboratory,
Presidency College,
Calcutta.

LIV. *On Transverse Oscillations of Beams under the Action of moving Variable Loads.* *By* Arnold N. Lowan, *Institute for Advanced Study, Princeton, N.J.**

THE problem of transverse oscillations of beams under the action of moving loads has been treated by S. Timoshenko [1] and C. E. Inglis [2] by the method of harmonic analysis in the particular case where the loads are moving along the beam with uniform velocity. For the general case of any arbitrarily prescribed law of motion a method of successive approximations has been given by H. H. Jeffcott [3].

The object of the present paper is to give a rigorous solution of the last named problem by the method presented in a number of earlier papers [4], [5].

The fundamental differential equation of the problem is

$$\frac{\partial^2 u}{\partial t^2} + a^2 \frac{\partial^4 u}{\partial x^4} = \frac{1}{m}\phi(x, t), \quad . \quad . \quad . \quad . \quad (1)$$

where m=mass per unit length,

E=modulus of elasticity,

I=moment of inertia of a cross-section with respect to its neutral axis,

a=value of $\frac{EI}{m}$,

$\phi(x, t)$=applied force per unit length of the beam,

l=length of the beam,

* Communicated by the Author.

u=transversal displacement,

x=distance along axis of beam,

t=time.

In the subsequent developments we will assume that the ends of the beam are freely supported, in which case the boundary conditions take the form

$$u(x,t)=\frac{\partial^2}{\partial x^2}u(x,t)=0 \text{ at } x=0 \text{ and } x=l. \quad . \quad . \quad (2)$$

In addition, the solution of (1) must satisfy the initial conditions

$$\lim_{t\to 0} u(x,t)=f(x), \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$\lim_{t\to 0} \frac{\partial}{\partial t}u(x,t)=g(x), \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $f(x)$ and $g(x)$ are the initial displacement and velocity distribution along the beam.

The general solution of the system (1) to (4) will be derived in terms of any arbitrary function $\phi(x,t)$. From this general solution it will then be possible to obtain the solution for the case of moving variable loads by suitably particularizing the function $\phi(x,t)$.

Consistently with the method employed in the papers above mentioned, we operate on the differential equation and the given boundary conditions by the Laplace operator L, defined by

$$\mathrm{L}\{u(x,t)\}=\int_0^\infty e^{-\lambda t}u(x,t)dt=y(x,\lambda),$$

$$\mathrm{L}\{\phi(x,t)\}=\int_0^\infty e^{-\lambda t}\phi(x,t)dt=\mathrm{Q}(x,\lambda).$$

If we make use of the identity *

$$\mathrm{L}\left\{\frac{\partial^2}{\partial t^2}\mu(x,t)\right\}=\lambda^2\mathrm{L}\{u(x,t)\}-\lambda u(x,0)-\left(\frac{\partial}{\partial t}u(x,t)\right)_{t=0}$$
$$=\lambda^2 y(x,\lambda)-\lambda f(x)-g(x),$$

the result of operating on (1) and (2) by the operator L yields the following system for the function $y(x,\lambda)$:

$$a^2\frac{\partial^4 y}{\partial x^4}+\lambda^2 y=\mathrm{Q}(x,\lambda)+\lambda f(x)+g(x), \quad . \quad . \quad (5)$$

$$y(x)=y''(x)=0 \text{ at } x=0 \text{ and } x=l. \quad . \quad . \quad . \quad (6)$$

* See reference (5).

The general solution of (5) and (6) may be written in the form

$$\left.\begin{aligned} y(x,\lambda) = &-\int_0^l G(x,\xi,\lambda)Q(\xi,\lambda)d\xi, \\ &-\int_0^l \lambda f(\xi)G(x,\xi,\lambda)d\xi, \\ &-\int_0^l g(\xi)G(x,\xi,\lambda)d\xi, \end{aligned}\right\} \quad . \quad . \quad . \quad (7)$$

where $G(x, \xi, \lambda)$ is the Green function corresponding to the homogeneous differential equation

$$a^2\frac{\partial^4 y}{\partial x^4}+\lambda^2 y=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

in conjunction with the boundary conditions (6). Let λ_n designate the characteristic values of the system (8) and (6), and $y_n(x)$ the corresponding normalized characteristic functions. Then we have, in the usual manner,

$$G(x,\xi,\lambda)=\sum_{n=1}^{\infty}\frac{y_n(x)y_n(\xi)}{\lambda_n^2-\lambda^2}, \quad . \quad . \quad . \quad . \quad (9)$$

or

$$G(x,\xi,\lambda)=-\sum_{n=1}^{\infty}\frac{z_n(x)z_n(\xi)}{\alpha_n^2+\lambda^2}, \quad . \quad . \quad . \quad (9')$$

where the α_n's are the characteristic values of the homogeneous differential equation

$$a^2\frac{\partial^4 z}{\partial x^4}-\lambda^2 z=0 \quad . \quad . \quad . \quad . \quad . \quad (8')$$

in conjunction with the boundary condition (6), and the z_n's are the corresponding normalized characteristic functions. With

$$\lambda^2=a^2\mu^4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

the general solution of (8') is

$$z(x)=A\sin\mu x+B\cos\mu x+C\sinh\mu x+D\cosh\mu x, \quad (11)$$

where A, B, C, and D are integration constants to be determined, so that (11) will satisfy the boundary conditions (6) and the normalizing condition

$$\int_0^l (z_n(x))^2 dx=1. \quad . \quad . \quad . \quad . \quad . \quad (12)$$

It is readily seen that

$$z_n(x)=\sqrt{\frac{2}{l}}\sin\mu_n x;\quad \mu_n=\frac{n\pi}{l};\quad \alpha_n=\left(\frac{n\pi}{l}\right)^2 a. \qquad (13)$$

From (7) we may write in a purely formal manner

$$\left.\begin{aligned} u(x,t)=\mathrm{L}^{-1}\{y(x,\lambda)\}=&-\int_0^l \mathrm{L}^{-1}\{\mathrm{G}(x,\xi,\lambda)\mathrm{Q}(\xi,\lambda)\},\\ &-\int_0^l \mathrm{L}^{-1}\{\lambda\mathrm{G}(x,\xi,\lambda)\}d\xi,\\ &-\int_0^l g(\xi)\mathrm{L}^{-1}\{\mathrm{G}(x,\xi,\lambda)\}d\xi. \end{aligned}\right\}. \qquad (14)$$

From (9′) we get

$$\mathrm{L}^{-1}\{\mathrm{G}(x,\xi,\lambda)\}=-\sum_{n=1}^{\infty} z_n(x)z_n(\xi)\frac{\sin\alpha_n t}{\alpha_n}=-\Gamma(x,\xi,t) \quad \text{(say)}$$
$$\ldots \qquad (15)$$

and
$$\mathrm{L}^{-1}\{\lambda\mathrm{G}(x,\xi,\lambda)\}=-\sum_{n=1}^{\infty} z_n(x)z_n(\xi)\cos\alpha_n t, \quad . \qquad (16)$$

as can be readily verified. Furthermore, by Borel's theorem*, we have

$$\left.\begin{aligned} \mathrm{L}^{-1}\{\mathrm{G}(x,\xi,\lambda)\mathrm{Q}(\xi,\lambda)\}&=\frac{1}{m}\int_0^t \phi(\xi,\eta)\Gamma(x,\xi,t-\eta)d\eta\\ &=-\frac{1}{m}\sum_{n=1}^{\infty}\frac{z_n(x)z_n(\xi)}{\alpha_n}\int_0^t \phi(\xi,\eta)\sin\alpha_n(t-\eta)d\eta. \end{aligned}\right\}. \qquad (17)$$

In view of the equations (12) and (15) to (17), our solution (14) becomes

$$\left.\begin{aligned} u(x,t)=&\frac{2}{lm}\sum_{n=1}^{\infty}\frac{\sin\frac{n\pi}{l}x}{\alpha_n}\int_0^l\int_0^t \sin\frac{n\pi\xi}{l}\phi(\xi,\eta)\sin\alpha_n(t-\eta)\,d\xi\,d\eta\\ &+\frac{2}{l}\sum_{n=1}^{\infty}\sin\frac{n\pi x}{l}\cos\alpha_n t\int_0^l f(\xi)\sin\frac{n\pi\xi}{l}\,d\xi\\ &+\frac{2}{l}\sum_{n=1}^{\infty}\frac{\sin\frac{n\pi\xi}{l}}{\alpha_n}\sin\alpha_n t\int_0^l g(\xi)\sin\frac{n\pi\xi}{l}\,d\xi. \end{aligned}\right\}$$
$$\ldots \qquad (18)$$

* See formula (9), A. N. L.

This is the complete solution of the problem of the transverse oscillations of a beam with freely supported ends under the action of impressed forces of magnitude $\phi(x,t)$, where the initial displacement and velocities are $f(x)$ and $g(x)$ respectively.

The first term in (18), to be subsequently designated $u_1(x,t)$, represents the forced vibration arising from the impressed forces, while the sum of the second and third terms represents the free vibrations, the natural frequency of which, in view of the significance of α_n from (13), is seen to depend on the geometrical shape of the beam and on its modulus of elasticity.

We shall illustrate the general formula (18) by deriving from it the solutions appropriate to the case of a freely supported beam traversed either by a system of concentrated moving loads or by a continuously distributed moving load. In both cases the velocity is assumed to be a prescribed function of time.

Case of Concentrated Loads.

From (18) it is apparent that if the impressed force $\phi(x,t)$ may be written in the form $\Sigma\phi_i(x,t)$, the corresponding solution may be obtained by superposition of the solutions corresponding to the individual ϕ_i's. It will therefore be sufficient to confine our attention to the case of a single concentrated load of magnitude $\phi(t)$ and moving with velocity $x=h(t)$.

Consider the double integral

$$\int_0^t \sin\alpha_n(t-\eta)\left\{\int_0^l \phi(\xi,\eta)\sin\frac{n\pi\xi}{l}\,d\xi\right\}d\eta.$$

For any particular value $t=t_1$ let $c=h(t_1)$. It is then clear that in the integral in brackets the actual region of integration reduces to the infinitesimal interval from $c-\epsilon$ to $c+\epsilon$, for which

$$\lim_{\epsilon\to 0}\int_{c-\epsilon}^{c+\epsilon}\phi(\xi,\eta)d\xi=\phi(t_1). \quad . \quad . \quad . \quad (19)$$

In view of (19) it follows at once

$$\int_0^l \phi(\xi,\eta)\sin\frac{n\pi\xi}{l}\,d\xi=\sin\frac{n\pi c}{l}\,.\phi(t_1)=\sin\frac{n\pi}{l}h(t_1)\,.\phi(t_1), \quad (20)$$

and, therefore, finally

$$u_1(x,t)=\frac{2}{lm}\sum_{n=1}^{\infty}\frac{\sin\frac{n\pi x}{l}}{\alpha_n}\int_0^t \phi(\eta)\,.\sin\alpha_n(t-\eta)\,.\sin\frac{n\pi}{l}h(\eta)\,.d\eta. \quad . \quad . \quad . \quad (21)$$

This is the general solution for the case of a load of magnitude $\phi(t)$ moving in accordance with the law of motion $x=h(t)$.

As an illustration let $h(t)=vt$ and $\phi(t)=\mathrm{P}\cos\omega t$. In this case (21) becomes

$$u_1(x,t)=\frac{2\mathrm{P}}{lm}\sum_{n=1}^{\infty}\frac{1}{\alpha_n}\sin\frac{n\pi x}{l}\int_0^t \sin\alpha_n(t-\eta)\sin\frac{n\pi v}{l}\eta\cos\omega\eta\,d\eta. \quad . \quad . \quad . \quad (22)$$

Making use of the identity

$$\sin a\sin b\cos c=\tfrac{1}{4}\{\cos(a-b+c)+\cos(-a+b+c) -\cos(a+b+c)-\cos(a+b-c)\}, \quad . \quad (23)$$

our solution (22) assumes the form

$$u_1(x,t)=\frac{\mathrm{P}}{lm}\sum_{n=1}^{\infty}\sin\frac{n\pi x}{l}\left\{\frac{\sin\left(\omega+\frac{n\pi v}{l}\right)t}{\alpha_n^2-\left(\omega+\frac{n\pi v}{l}\right)^2}+\frac{\sin\left(\frac{n\pi v}{l}-\omega\right)t}{\alpha_n^2-\left(\omega-\frac{n\pi v}{l}\right)^2}\right\} \quad . \quad (22')$$

$$-\frac{\mathrm{P}v}{\pi ma}\sum_{n=1}^{\infty}\frac{1}{n}\sin\frac{n\pi x}{l}\left\{\frac{\sin\alpha_n t}{(\omega+\alpha_n)^2-\left(\frac{n\pi v}{l}\right)^2}+\frac{\sin\alpha_n t}{(\omega-\alpha_n)^2-\left(\frac{n\pi v}{l}\right)^2}\right\}$$

The identity of (22′) with the solution given by Timoshenko can be seen at a glance. For $\omega=0$ (22′) yields at once the solution corresponding to the case of a concentrated load of constant magnitude, and moving with uniform velocity.

Case of continuously distributed Loads.

Let $y=\phi(x)$ be the analytical expression corresponding to a continuously distributed load extending over an interval of length c, at the moment $t=0$ when this interval starts at $x=0$. At the time when the load has traversed a distance γ the solution $u_1(x,t)$ assumes the form

$$u_1(x,t)=\frac{2}{lm}\sum_{n=1}^{\infty}\frac{1}{\alpha_n}\sin\frac{n\pi x}{l}\int_0^t \sin\alpha_n(t-\eta)\left\{\int_\gamma^{\gamma+c}\phi(\xi-\gamma)\sin\frac{n\pi\xi}{l}\,d\xi\right\}d\eta. \quad (24)$$

The desired solution for the forced vibration can evidently be obtained from (24) by replacing γ by $\gamma(\eta)$ where $x=\gamma(t)$ is the prescribed law of motion of the load. Thus, in this case,

$$u_1(x,t)=\frac{2}{lm}\sum_{n=1}^{\infty}\frac{1}{\alpha_n}\sin\frac{n\pi x}{l}\int_0^t \sin\alpha_n(t-\eta)\left\{\int_{\gamma(\eta)}^{c+\gamma(\eta)}\phi(\xi-\gamma(\eta))\sin\frac{n\pi\xi}{l}\,d\xi\right\}.d\eta. \quad (25)$$

In particular, if we are dealing with a uniformly distributed load then $\phi(x)=P=\text{const.}$ and the second integral becomes

$$P\int_\gamma^{\gamma+c}\sin\frac{n\pi\xi}{l}\,d\xi=\frac{2Pl}{n\pi}\sin\frac{n\pi c}{2l}\sin\left(\frac{c}{2}+\gamma\right)\frac{n\pi}{l}.$$

The solution (25) therefore becomes

$$u_1(x,t)=\frac{4P}{m\pi}\sum_{n=1}^{\infty}\frac{1}{n\alpha_n}\sin\frac{n\pi x}{l}\sin\frac{n\pi c}{2l}\int_0^t \sin\alpha_n(t-\eta)\times\sin\frac{n\pi}{l}\left[\frac{c}{2}+\gamma(\eta)\right]d\eta. \quad (26)$$

In both the general case (25) and the particular case (26) the given solutions are valid only up to the time t_1, when the right end of the load has reached $x=l$; in other words, $\gamma(t_1)=l-c$. If t_2 is the time at which the left end of the load reaches $x=l$; in other words, if $\gamma(t_2)=l$, it is clear that in the interval of time between t_1 and t_2 the solution may be obtained from (25) by replacing the upper limit $c+\gamma(\eta)$ by l.

It is clear that the general formula (18) is equally applicable to the case of stationary loads of constant or fluctuating magnitude. Consequently, the theory above presented, and summarized in formulæ (18), (21), and (25), will yield the transverse vibrations of a beam under the combined influence of stationary concentrated or continuously distributed loads (of constant or fluctuating magnitude), in conjunction with any system of concentrated or continuously distributed loads which traverse the beam with velocities which are prescribed functions of time.

Bibliography.

(1) S. Timoshenko, Phil. Mag. xliii. p. 1018 (1922).
(2) C. E. Inglis, Inst. C.E. Minutes of Proc. ccxviii. (1914).
(3) H. H. Jeffcott, Phil. Mag. ser. 7, viii. pp. 66–97 (1929).
(4) A. N. Lowan, "On the Cooling of a Radioactive Sphere," Phys. Rev. (Nov. 1, 1933). This paper will be referred to as A. N. L.
(5) A. N. Lowan, "Operational Treatment of certain Mechanical and Electrical Problems," Phil. Mag. (June 1934).

LV. *Note on the Clock Problem in Relativity.* By J. W. Campbell, *Ph.D.* *.

IN discussing the problem of the relative flow of time for two observers who separate and meet again Eddington † has given considerable prominence to disturbances as determining factors in the problem. Disturbances are absolute, it is true, and the contrast between undisturbed and disturbed motion plays an important rôle in relativity, but it is the purpose of this note to show that they do not constitute a fundamental criterion in the clock problem. In the particular case which Eddington has discussed a body B was projected from the earth and returned to find that he had lived a *shorter* time than a body A which remained on the earth undisturbed, but it will be shown that B could be disturbed in such a way as to leave the earth and return to find

* Communicated by the Author.

† 'The Mathematical Theory of Relativity,' revised edition (1930), Supplementary Note, §1, p. 241.

that he had lived a *longer* time than A who had remained on the earth.

We first prove two propositions :—

1. *Time is increased over some Disturbed Paths.*

Consider a particle which is distant r from a mass m. For such a particle the world interval is given by

$$ds^2 = -\gamma^{-1}dr^2 - r^2 d\theta^2 - r^2 \sin^2\theta d\phi^2 + \gamma c^2 dt^2, \quad . \quad (1)$$

where $\gamma = 1 - 2m/r$ and c is the velocity of light. Also ds/c is the interval of time for a clock moving with the particle, and for $dr = d\theta = d\phi = 0$ and $r = \infty$ we have $ds = c\,dt$. Therefore t is the time of a clock which is far removed from m and which is at rest relative to m. Equation (1) may therefore be regarded as giving the clock rate of a particle moving about m as seen by an observer who is far remote from m and at rest relative to m.

Including only quantities up to the first order in $1/c^2$, this equation may be written

$$ds^2 = \left(1 - \frac{v^2}{c^2} - \frac{2m}{r}\right) c^2 dt^2, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where v is the speed of the particle, and therefore

$$ds = \left(1 - \frac{v^2}{2c^2} - \frac{m}{r}\right) c\,dt. \quad . \quad . \quad . \quad . \quad (3)$$

Hence the lag in time for the particle, on the standard of the distant observer, is

$$\int_{t_1}^{t_2} \left(\frac{v^2}{2c^2} + \frac{m}{r}\right) dt. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Now in the classical theory of mechanics if a particle moves about a body of mass M in an orbit of semi-major axis a and eccentricity e, then *

$$\left.\begin{aligned} r^2 \frac{d\theta}{dt} &= k\{\mathrm{M}a(1-e^2)\}^{\frac{1}{2}}, \\ v^2 &= k^2\mathrm{M}\left(\frac{2}{r} - \frac{1}{a}\right), \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (5)$$

where k^2 is the constant of gravitation.

* F. R. Moulton, ' Celestial Mechanics,' p. 149.

For such a particle, expression (4) becomes

$$\int_{t_1}^{t_2}\left(\frac{k^2\mathrm{M}}{r^2c^2}-\frac{k^2\mathrm{M}}{2ac^2}+\frac{m}{r}\right)dt, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and this will be the value of the lag in the relativity orbit if only first order quantities in $1/c^2$ are included.

Now m is mass in the relativity sense of a length and so we may write $m=\mathrm{M}k^2/c^2$. Also let us take $t_2-t_1=\mathrm{P}$, the period of the revolving particle. Then by using (5) we may readily show that (4) becomes

$$\frac{3k^2\mathrm{MP}}{2c^2a} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Expression (7) is thus the lag of time for the particle in one revolution.

Let us next consider the motion of the particle revolving about m to be disturbed in the following manner :—

Suppose that when the particle is passing through periastron it is given an impulse in the direction of its motion. Then it will thereafter move in an ellipse of major axis $2a'$, where $a'>a$, but the distance from m of its periastron passage will remain unaltered. It will also have a period P', where $\mathrm{P}'>\mathrm{P}$.

Suppose P and P' are commensurable and such that $n\mathrm{P}=n'\mathrm{P}'$, where n and n' are positive integers relatively prime. Then at a time $\mathrm{N}n'\mathrm{P}'$ after the impulse, where N is any positive integer, the particle will again be at periastron. At such an instant let us suppose it is given a second impulse so as to reduce its periastron speed to its original value. It will then follow a path identical with its original orbit, except for the change of orientation due to the relativity advance of periastron.

Now although we may regard the effects of the disturbances (impulses) on the proper time of the particle as being unknown, we may for a given type of impulse regard them as definite. Suppose then that the particle's clock makes gains of ϵ_1 and ϵ_2 by reason of the two impulses, respectively, where both ϵ_1 and ϵ_3 are arbitrary but definite in both magnitude and sign.

Then from expression (7) it follows that between the instant just before the first impulse and the instant just after the second impulse the particle's clock gains an amount

$$\epsilon_1-\frac{3k^2\mathrm{M}}{2c^2a'}.\mathrm{N}n'\mathrm{P}'+\epsilon_2$$

If the particle had not been disturbed its gain in the same interval would have been

$$-\frac{3k^2M}{2c^2a}.Nn'P'.$$

Therefore if we put

$$\epsilon_3=\frac{3k^2Mn'P'}{2c^2}\left(\frac{1}{a}-\frac{1}{a'}\right),$$

the proper time of a particle on the disturbed orbit will exceed the proper time on the undisturbed orbit by

$$\epsilon_1+N\epsilon_2+\epsilon_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Now since $a'>a$, ϵ_3 is definitely positive and since N may be taken large at pleasure we may, by taking N sufficiently large, make expression (8) positive no matter what the values of ϵ_1 and ϵ_2. We have here then a whole series of disturbed orbits such that in each case the proper time in the disturbed orbit is greater than that in the undisturbed orbit.

It should be noted, moreover, that this result is not inconsistent with the principle that the proper time of a particle following a natural path is greater than the proper time for any neighbouring disturbed path. The paths in the above instance are not neighbouring, for even though for small impulses they are neighbouring in the space of the distant observer they are not neighbouring in space-time.

2. *The Explicit Effect of Disturbances themselves on Time is Zero.*

In the first of my former two papers * on the clock problem the motion of one body observed was given by the equations

$$\ddot{x}=\ddot{x}_1+\frac{\partial U}{\partial y}, \quad \ddot{y}=\ddot{y}_1+\frac{\partial U}{\partial x}, \quad \ddot{z}=\ddot{z}_1+\frac{\partial U}{\partial z},$$

where (x, y, z) was the position of the body, U was the potential at its position, and $(\ddot{x}_1, \ddot{y}_1, \ddot{z}_1)$ was the acceleration produced by other causes, *i. e.*, disturbances. The lag of time, however, was not an explicit function of $\ddot{x}_1$,

* Phil. Mag. (7) xv. p. 48 (January 1933) ; and xvi. p. 529 (September 1933).

$\ddot{y}_1$, and $\ddot{z}_1$. It was a function of the velocity and of the potential, and was a function of the disturbances only in so far as these entered implicitly through the velocity.

Again in the second paper when one observer A remained at rest in an inertial frame while another B moved off along a radial straight line from A and back again, the lag of B's time, whether from the point of view of A or of B, was a function of B's velocity alone and in no way dependent upon his acceleration explicitly.

The explicit effect of disturbances on time is therefore zero, and so only their implicit effect through the velocity need be allowed for. Thus while proposition 1 is true irrespective of the values of ϵ_1 and ϵ_2, the values of ϵ_1 and ϵ_2 are actually zero.

Now suppose B's excursion from the earth is made as follows :—

With the earth at perihelion B is disturbed so as to follow a cometary orbit with perihelion distance equal to the perihelion distance of the earth, and with longitude of perihelion sufficiently different from that of the earth so that the earth would not appreciably perturb B's motion on subsequent near approaches, and at some later approach it is again projected to the earth at a perihelion passage.

Then consider the effects of the factors : —

(1) the sun's gravitational field,

(2) the earth's gravitational field,

(3) the (projecting) disturbances on B,

(4) the disturbances (molecular bombardments by the earth) on A.

Proposition 1 shows that due to (1) and (3) alone B will live a longer time than A. The effect of (2) alone is to accentuate this result, for it will retard A's time without appreciably affecting B's. And, lastly, by proposition 2 the explicit effect of (4) is zero, while the implicit effect is allowed for in the motion of the earth. The sum total result is therefore that in such a case the disturbed body B lives a longer time than the body A which remained on the earth.

Some assistance may be had in accounting for this result by noting the following :—

If a particle describes a closed orbit of semi-major

axis a about a mass M with period P, then from (4), (6), and (7) its lag of time in one revolution is made up of

(a) an amount

$$\int_{t_1}^{t_2} \frac{v^2}{2c^2}\,dt = \frac{k^2\mathrm{MP}}{2c^2a}$$

due to the speed, and

(b) an amount

$$\int_{t_1}^{t_2} \frac{m}{r}\,dt = \frac{k^2\mathrm{MP}}{c^2a}$$

due to the presence of the gravitational field about M. Hence the explicit effect (b) of the gravitational field is twice as great as its implicit effect (a). Also if the particle followed the same orbit as its undisturbed orbit about M but with M absent, and the kinematical motion kept the same by suitable constraints, then the lag in one revolution would be given by (a) alone. That is, the lag of time in a given gravitational orbit is greater than in the same orbit kinematically described in the same manner due to suitable constraints by the factor 3.

University of Alberta.
September 1934.

LVI. *Notices respecting New Books.*

The Electronic Structure and Properties of Matter. By C. H. Douglas Clark. [Pp. 374+xxv.] (Chapman & Hall, Ltd. Price 21*s.* net.)

IN this the first volume of "a comprehensive treatise of atomic and molecular structure" the author has already cast his net wide. Part I. contains a survey of the electronic structure of atoms in relation to the Periodic Classification, Line Spectra, Valency, and Chemical Combination. Part II. considers a wide range of physical properties of atoms, molecules, and aggregates.

The nature of the treatment may perhaps best be indicated by noting that there are references to something like a thousand original papers, the titles of which are very sensibly grouped at the end of the appropriate chapter. Such thoroughgoing comprehensiveness has its obvious value, but the exigencies of space often necessitate the briefest consideration of much

of the work cited. Brevity is seldom associated with clarity, and in escaping the difficult task of selection and the still more difficult one of critical discussion Mr. Clark has not always avoided the danger of obscurity.

To give one example only: London's theory of linkages is summarized in the following words:—"The essential point of the theory may be expressed (in terms of the wave mechanics) by the statement that molecular stability is conditioned by corresponding solutions of Schrödinger's wave equation applied to the particular case having the type of symmetry required by Pauli's exclusion principle." No other reference is made in this volume to wave mechanics.

The introduction to entropy is not at all clear, and the definition of coefficient of expansion is inexact.

The book contains, however, a great deal of value. There are 48 tables and many graphs, summarizing in a readily appreciated way much information. No doubt many research workers will find a handy guide to the sort of things that have been said and done in the fields covered.

Introduction à la Théorie des Groupes et à ses Applications à la Physique Quantique. By EDMOND BAUER. [Pp. 170.] (Les Presses Universitaires de France, Paris, 1933. Price 40 fr.)

THE rapid development of quantum mechanics has made the mathematical training given to students of physics inadequate. Until recently the calculus was their chief need, but now a considerable knowledge of advanced algebra—the theory of groups and matrices—is equally necessary. In consequence a number of books have appeared which contain, along with the elements of quantum theory, the mathematical foundations necessary for its development. The one under review contains an attempt to simplify the presentation of the subject, partly by reserving some of the more difficult parts for a second volume, which is stated to be in preparation.

The chapters of this volume are ordered similarly to those of the standard text of H. Weyl. The first discusses unitary geometry, introducing matrices and Hermitian forms and operators. The second, centred round Schrödinger's wave equation, introduces the principles of quantum mechanics, and leads up to the remarkable generalization, due to Schrödinger, Dirac, and Jordan, that "a physical magnitude is an operator applied to a wave function." In the third, groups, subgroups, etc. are defined, and the theory of the representations of a group by means of the linear transformation group is obtained. This leads to the Jordan theorem on the uniqueness of the composition series of a group and is followed by

a discussion of group characteristics. The fourth and fifth chapters contain the applications of group theory to the wave-equation, the latter chapter giving in some detail the consequences of the invariance of the equation under the transformations of the rotation group.

This is a sound and attractive introduction to the subject, but readers who have no previous acquaintance with the theory of matrices may still find difficulty with the opening chapter; it might be useful to read it in parallel with Weyl's treatise. Mathematicians familiar with the theory of projective invariants will notice with interest the important rôle played by Gordan's series in the theory of spectra. Weyl remarks that it is the "fundamental mathematical formula for the classification of atomic spectra and for the theory of the valency bond."

There is no index, and the need is only met in part by a detailed table of contents.

Theoretical Physics. By GEORG JOOS. Translated from the first German edition by IRA M. FREEMAN. [Pp. xxiii+748.] (Blackie: London and Glasgow, 1934. Price 25*s*.)

THE aim of the author is that this book shall serve as a guide to practically the whole field of theoretical physics. The reader is conducted not, indeed, to the highest peaks, but to "an intermediate plateau from which the summits are visible and not too difficult to attain." In traversing the ground well proven routes are not despised, but many new and more convenient ones are opened up; and the relation between the parts and the whole is emphasized by the well-arranged plan of the journey. To have covered so much ground in a single volume without superficiality, with continuous clarity of exposition and with a discernment which reveals the interest in what are often regarded as the more barren tracts, is a remarkable achievement.

The book is divided into seven parts. The first two—mathematical introduction, which includes an admirable account of vector calculus, which is used throughout the book, and mechanics—occupy about a third of the book. Electromagnetic phenomena are treated in two parts, the first dealing with field theory (including optical phenomena), the second with atomic theory. Heat is similarly divided into a phenomenological and a statistical part. The final part of the book deals with the structure of atoms and molecules, and includes a new chapter (as compared with the original German edition) on nuclear physics. There are a considerable number of examples, which extend the scope of the text, and a useful list of general references.

The account of statistical mechanics, including as it does a fairly detailed treatment of the Bose and Fermi statistics, will be of particular value, as there is a surprising dearth of books which attempt to bridge the gap between an elementary classical treatment and the modern developments which are at the basis of some of the most interesting and important recent investigations in theoretical physics.

The picture of physical science presented by a book of this kind is necessarily incomplete, for the experimental side, in virtue of which the theoretical scheme gains its primary significance, is virtually ignored. Further, by the presentation of the finished product of theoretical investigation, with a minimum of reference to the historical course of development which has led up to it, an erroneous impression of the character of physical theory may be given. This book, therefore, which deals with a limited aspect of a wide range of subject-matter, cannot replace those which deal with a more limited range of subject-matter from a broader standpoint; but it will be invaluable as a supplement to them. It is a masterpiece of clear and concise exposition, rendered possible by the author's penetrating grasp of essentials, and it may be strongly recommended to physicists, whether as students, research workers, or teachers.

The publishers are to be congratulated on the high standard of production of the book at so reasonable a price. The translation has been well carried out, in that, while it is not slavishly literal, the temptation to unduly free paraphrase has been resisted, so that the style of the author is faithfully reflected.

The Electronic Theory of Chemistry. An Introductory Account. By R. F. Hunter. [Pp. vi+125.] (Arnold, 1934. Price 8*s.* 6*d.*)

This is a monograph in which the author gives an account of the results which have been obtained during the last decade in the application of the electronic theory of valency to the problems of molecular structure and valency, and also to the relations disclosed by the systematic investigation of well-known general reactions in the field of organic chemistry. The success achieved by the electronic theory in its applications to such problems constitutes one of the most outstanding advances which have yet been made in the systemization of a large variety of established facts.

The clear and concise account presented by Professor Hunter should be of great value not only to more advanced students but also to those whose general outlook on fundamental problems was largely acquired in the pre-electronic period.

The characteristic features attributable to electro-valency and to co-valent, coordinate, and singlet linkages are described in a simple and attractive fashion, and the problems associated with aromatic substitution, side-chain reactivity, tautomerism, and conjugation have provided the author with excellent material to illustrate the great advantages of the electronic theory in the interpretation of fundamental types of reaction familiar to the student of organic chemistry.

The text is not free from minor blemishes. The statement on p. 46 that sodium acetate, like sodium chloride, is 80 per cent. dissociated will not be accepted by the physical chemist, who may also object with considerable justification to the assertion (p. 48) that co-valent hydrogen chloride becomes electro-valent when dissolved in water.

The Endless Quest—Three Thousand Years of Science. By F. W. Westaway. [Pp. 1080+xix, with 193 figs. and 48 plates.] (Blackie & Son, Ltd. Price 21*s.*)

Mr. Westaway is a professional philosopher, and one whose interests in the results, methods, and underlying philosophy of science fit him peculiarly well for the writing of a book of this character. To some readers his literary style may possibly seem a little discursive, but that is rather an advantage than otherwise, for the reader is certainly led along as easy and smooth a path as possible—the difficulties may appear, but only to vanish again almost at once.

It is hardly a book for the pocket—it is not even one to hold in the hand for long, for there are 1100 pages with 55 chapters and numerous illustrations within which the author has packed a most comprehensive collection of essays on a great variety of subjects within the 'Endless Quest.' Mathematics, Physics, Chemistry, Astronomy, Geology, Meteorology, Biology, Anthropology, Archæology, Agriculture, Hygiene, Medicine, Philosophy, all find place. And even that is not all, for special chapters are provided on Philosophy and Science, Causation and Indeterminancy, Hypotheses, Idealism, and other mysteries in Physics (a delightful chapter by the way, wisely consisting mainly of relevant and other quotations from well-known scientific writers). It will not do to omit reference to the first thirty-six chapters of about 400 pages which are devoted to a history of science from the ancient world to the modern—and a very good history too.

Of this book it may be true to say schoolboys will read it with some profit, laymen with much profit, professional scientists with most profit.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]